

FORM PTO 156 (REV. 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY DOCKET NUMBER 2002-0056A
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371		
International Application No. PCT/JPO0/04888	International Filing Date July 21, 2000	Priority Date Claimed July 21, 1999
Title of Invention POLYMER CONTAINING TRIPHENYLBORON AND USE THEREOF		
Applicant(s) For DO/EO/US Masaaki YOSHIMARU, Masanori KOHARA, Yoshifumi SHIBUYA		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. §371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. §371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. §371(c)(2)). ATTACHMENT A 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)). a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19. 9. <input checked="" type="checkbox"/> An <u>unexecuted</u> oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). ATTACHMENT B 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)). Items 11. to 14. below concern other document(s) or information included: 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. ATTACHMENT C 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. ATTACHMENT D - Substitute Specification, Claims and Abstract (56 pages) <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> Other items or information:		

THE COMMISSIONER IS AUTHORIZED
TO CHARGE ANY DEFICIENCY IN THE
FEE FOR THIS PAPER TO DEPOSIT
ACCOUNT NO. 23-0975.

U.S. APPLICATION NO. 10/031618		INTERNATIONAL APPLICATION NO. PCT/JP00/04888	ATTORNEY'S DOCKET NO. 2002_0056A																
15. <input checked="" type="checkbox"/> The following fees are submitted		CALCULATIONS PTO USE ONLY																	
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 International Search Report has been prepared by the EPO or JPO \$ 890.00 International preliminary examination fee not paid to USPTO but international search paid to USPTO \$ 740.00 International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00 International preliminary examination fee paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 100.00																			
ENTER APPROPRIATE BASIC FEE AMOUNT =																			
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Claims</th> <th style="text-align: left; padding: 2px;">Number Filed</th> <th style="text-align: left; padding: 2px;">Number Extra</th> <th style="text-align: left; padding: 2px;">Rate</th> </tr> </thead> <tbody> <tr> <td style="text-align: left; padding: 2px;">Total Claims</td> <td style="text-align: left; padding: 2px;">-20 =</td> <td style="text-align: left; padding: 2px;"></td> <td style="text-align: left; padding: 2px;">X \$18.00</td> </tr> <tr> <td style="text-align: left; padding: 2px;">Independent Claims</td> <td style="text-align: left; padding: 2px;">- 3 =</td> <td style="text-align: left; padding: 2px;"></td> <td style="text-align: left; padding: 2px;">X \$84.00</td> </tr> <tr> <td colspan="3" style="text-align: left; padding: 2px;">Multiple dependent claim(s) (if applicable)</td> <td style="text-align: left; padding: 2px;">+ \$280.00</td> </tr> </tbody> </table>				Claims	Number Filed	Number Extra	Rate	Total Claims	-20 =		X \$18.00	Independent Claims	- 3 =		X \$84.00	Multiple dependent claim(s) (if applicable)			+ \$280.00
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Total Claims	-20 =		X \$18.00																
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TOTAL OF ABOVE CALCULATIONS =																			
<input type="checkbox"/> Small Entity Status is hereby asserted. Above fees are reduced by 1/2. SUBTOTAL =																			
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). TOTAL NATIONAL FEE =																			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40 per property + TOTAL FEES ENCLOSED =																			
<input type="checkbox"/> A check in the amount of \$890.00 to cover the above fees is enclosed. A duplicate copy of this form is enclosed. <input type="checkbox"/> Please charge my Deposit Account No. 23-0975 in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed. <input type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0975</u> .																			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.																			
19. CORRESPONDENCE ADDRESS		By: <u>Warren Cheek</u> Warren M. Cheek, Jr., Registration No. 33,367 WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006-1021 Phone: (202) 721-8200 Fax: (202) 721-8250 January 22, 2002																	
000513 PATENT TRADEMARK OFFICE																			

[CHECK NO.: 48458]
 [2002_0056A]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Masaaki YOSHIMARU et al.

Attn: **BOX PCT**

Serial No. NEW

Docket No. 2002_0056A

Filed January 22, 2002

POLYMER CONTAINING TRIPHENYLBORON
AND USE THEREOF[Corresponding to PCT/JP00/04888
Filed July 21, 2000]**PRELIMINARY AMENDMENT**Assistant Commissioner for Patents,
Washington, DC 20231

Sir:

(Prior to calculating the filing fee) please amend the above-identified application as follows:

IN THE SPECIFICATION AND CLAIMS

Cancel without prejudice pages 1-71 of the English translation of the originally filed international application, submitting concurrently herewith as Attachment A, and substitute therefor the attached substitute specification and claims consisting of pages 1-56 including claims 1-10.

ATTACHMENT D

In addition, please amend the substitute specification and claims as follows:

Page 1, immediately after the title, please insert:

This application is a 371 of PCT/JP00/04888 filed July 21, 2000.

IN THE CLAIMS

7. (Amended) A composition comprising the polymer of claim 1.

8. (Amended) A composition comprising the polymer of claim 1 together with at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

9. (Amended) A fouling preventive comprising the polymer of claim 1.

10. (Amended) A fouling preventive comprising the polymer of claim 1 together with at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

Please add the following new claims:

11. (New) A composition comprising the polymer of claim 2.

12. (New) A composition comprising the polymer of claim 3.

13. (New) A composition comprising the polymer of claim 4.

14. (New) A composition comprising the polymer of claim 5.

15.(New) A composition comprising the polymer of claim 6.

16 (New) A composition comprising the polymer of claim 7.

REMARKS

Submitted herewith as Attachment A is an English translation of the international application as originally filed. The entire specification and claims consisting of pages 1-71 of the English translation have been replaced with the substitute specification and claims consisting of pages 1-56 and including claims 1-10, which substitute specification and claims correspond to the substitute specification and claims presented during prosecution of the international application by way of amendment under PCT Article 34 filed on February 19, 2001.

To the substitute specification, amendments have been effected to note the national stage status of the present application. In addition, the multiple dependencies of the claims have been removed to reduce the PTO filing fee, as well as to remove the improper multiple dependencies.

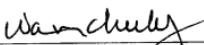
Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached pages are captioned "**Version with markings to show changes made**".

Favorable action on the merits is solicited.

Respectfully submitted,

Masaaki YOSHIMARU et al.

By


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Registration No. 33,367
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January 22, 2002

JC13 Rec'd PCT/PTO 22 JAN 2002

SPECIFICATION

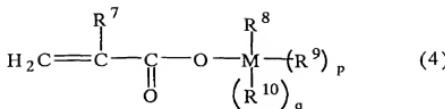
This application is a 371 of PCT/JP00/04388 filed July 21, 2000.
Technical Field

The present invention relates to a polymer containing triphenylboron and use thereof. More particularly, this invention relates to a preventive of fouling due to adhesion of aquatic fouling organisms (hereinafter to be also referred to as a fouling preventive), such as an antifouling agent for a fishnet, that prevents aquatic fouling organisms from adhering to and growing on culture and fixed fishnets, an underwater antifouling coating (e.g., ship bottom antifouling coating) that prevents aquatic fouling organisms from adhering to and growing on the bottom of a ship, a material used for a fishnet (e.g., buoy and rope), and condenser water channels of a nuclear energy or thermal power plant, and the like.

Background Art

When aquatic organisms such as coelenterates (e.g., hydrozoas, obelia etc.), shellfish, tubicolous polychaetes, algae, Polyzoa, Mollusca and the like adhere to the bottom of a ship, culture and fixed fishnets and the like, they cause a great economic loss to the ship and fishnets. Therefore, these aquatic organisms are called aquatic fouling organisms. For example, when barnacle and the like adhere to fishnets, the gaps are filled up. This may decrease oxygen in water by blocking the flow of tide, causing death of cultured fish from suffocation, or increase wave resistance, causing breakage and the like of the net when typhoon comes.

When these aquatic fouling organisms adhere to the ship bottom, the driving efficiency of the ship is decreased and fuel efficiency is decreased, which in turn results in economic loss. In an attempt to decrease the economic loss caused by the fouling organisms, therefore, great labor and cost have been expensed for the maintenance of objects susceptible to fouling, as the situation stands.



wherein R^7 is hydrogen atom or alkyl group having 1 to 4 carbon atoms; M is metal atom or silicon atom; when M is metal atom, R^8 , R^9 and R^{10} are the same or different and each is organic acid residue, when M is silicon atom, R^8 , R^9 and R^{10} are the same or different and each is alkyl group having 1 to 18 carbon atoms, aryl group or cycloalkyl group; when M is divalent metal atom, p and q are both 0, when M is trivalent metal atom, p is 1 and q is 0, and when M is quaternary metal atom, both are 1.

10

6. The polymer of claim 5, wherein the metal atom is zinc, copper or magnesium.

(Amended)

7. A composition comprising the polymer of ~~any of~~ claims 1-6.

15

(Amended) 8. The composition of claim 7, further comprising at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

20

(Amended)

9. A fouling preventive comprising the polymer of ~~any of~~ claims 1-6.

(Amended) 10. The fouling preventive comprising the polymer of Claim 1 together with

10. The fouling preventive of claim 9, which further comprises at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

SPECIFICATION

POLYMER CONTAINING TRIPHENYLBORON AND USE THEREOF

Technical Field

The present invention relates to a polymer containing triphenylboron and use thereof. More particularly, this invention relates to a preventive of fouling due to adhesion of aquatic fouling organisms (hereinafter to be also referred to as a fouling preventive), such as an antifouling agent for a fishnet, that prevents aquatic fouling organisms from adhering to and growing on culture and fixed fishnets, an underwater antifouling coating (e.g., ship bottom antifouling coating) that prevents aquatic fouling organisms from adhering to and growing on the bottom of a ship, a material used for a fishnet (e.g., buoy and rope), and condenser water channels of a nuclear energy or thermal power plant, and the like.

Background Art

When aquatic organisms such as coelenterates (e.g., hydrozoas, obelia etc.), shellfish, tubicolous polychaetes, algae, Polyzoa, Mollusca and the like adhere to the bottom of a ship, culture and fixed fishnets and the like, they cause a great economic loss to the ship and fishnets. Therefore, these aquatic organisms are called aquatic fouling organisms. For example, when barnacle and the like adhere to fishnets, the gaps are filled up. This may decrease oxygen in water by blocking the flow of tide, causing death of cultured fish from suffocation, or increase wave resistance, causing breakage and the like of the net when typhoon comes.

When these aquatic fouling organisms adhere to the ship bottom, the driving efficiency of the ship is decreased and fuel efficiency is decreased, which in turn results in economic loss. In an attempt to decrease the economic loss caused by the fouling organisms, therefore, great labor and cost have been expensed for the maintenance of objects susceptible to fouling, as the situation stands.

Various researches and suggestions have been heretofore made to prevent adhesion of aquatic fouling organisms. From the practical viewpoint, use of a series of organic tin compounds is effective. However, the organic tin compounds generally have strong toxicity to the extent that careless handling of products containing them can result in hazardous influence on the operator and that the environment may be contaminated.

These difficulties have produced the demand for a low-pollution preventive of fouling due to adhesion of aquatic fouling organisms, or an antifouling preventive, such as a low-pollution antifouling agent for a fishnet and a low-pollution underwater antifouling coating (e.g., ship bottom antifouling coating etc.). For example, JP-B-10849/1976 discloses an underwater antifouling coating containing a benzothiazole compound as an active ingredient; JP-A-38306/1985, JP-A-284275/1988 and JP-B-11606/1989 disclose various antifouling agents for fishnet and antifouling coating compositions, wherein a tetraalkyl thiuram disulfide compound and other compounds are combined; JP-B-50984/1986 discloses an anticontaminant agent for marine structures, which comprises a 3-isothiazolone compound as an active ingredient; and JP-B-20665/1989 and JP-B-24242/1990, and JP-A-9320/1978, JP-A-201804/1993, JP-A-100405/1994 and JP-A-100408/1994 disclose underwater antifouling coatings containing a maleimide compound as an active ingredient.

However, all of these antifouling agents only have a weak adhesion-preventive effect against coelenterates, such as hydrozoas, obelia and the like, and could not be used in a sea area where coelenterates live, such as the coasts of Tohoku region and Hokkaido. In Tokai and West Japan sea areas where lots of shellfish (e.g., barnacle, mussel etc.) and tubicolous polychaetes (e.g., *Hydrooides norvegica* etc.) live, moreover, the conventional antifouling agents show weak adhesion

preventive effects and cannot effectively prevent adhesion of these aquatic fouling organisms.

It is conventionally known that cuprous oxide is effective against shellfish, and organic copper type antifouling agents (e.g., copper pyrithion etc.) have been confirmed to be effective against shellfish and tubicolous polychaetes. However, cuprous oxide only shows a weak adhesion preventive effect against shellfish and tubicolous polychaetes. In addition, an organic copper group antifouling agent often thickens or gelates a coating upon mixing with the coating, thereby posing a defect that mixing with a coating is difficult.

In addition, JP-A-8-295608 discloses a fishnet antifouling agent containing a triphenylboron alkylamine adduct compound as an active ingredient, JP-A-8-295609 discloses a solution containing a triphenylboron octadecylamine adduct compound, and WO98/33892 discloses a triphenylboron-containing allylamine type polymer. However, sustained release of the active ingredient is difficult, and an antifouling effect cannot be maintained over a long time. Moreover, JP-A-11-20 199801 discloses a triarylboron-containing polymer and JP-A-11-302571 discloses a resin bonded with a trisubstituted boron-containing-amine complex.

The present invention aims at solving the above-mentioned defects and providing an antifouling component exhibiting a superior adhesion-preventive effect against aquatic fouling organisms such as coelenterates, shellfish, tubicolous polychaetes and the like and a fouling preventive containing this component, which is capable of retaining the effect for a long time.

The present invention also aims at providing an antifouling component superior in miscibility with other antifouling components, coating resins and the like, having a binder function and causing less adverse influence on the environment, and a fouling preventive containing this component.

Disclosure of the Invention

The present inventors have made intensive studies with the purpose of overcoming the above-mentioned various defects found in conventional fouling preventives, such as fishnet 5 antifouling agent, underwater antifouling coating and the like, and invented a novel polymer containing triphenylboron and a fouling preventive containing the same, that are associated with less possibility of environmental pollution, and show superior adhesion-preventive effects against aquatic fouling 10 organisms for a long time. That is, the present inventors have found that a novel triphenylboron-containing polymer shows a superior adhesion-preventive effect for a long time against coelenterates such as hydrozoas, obelia etc., shellfish such as barnacle, blue mussel, oyster, Serpula etc., tubicolous 15 polychaetes such as *Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc., and other aquatic fouling organisms, which resulted in the completion of the present invention.

The polymer containing triphenylboron of the present 20 invention has a triphenylboron-containing constituting unit, and has, in the same molecule, a resin moiety having a coating film-forming capability. Therefore, it can function not only as an active ingredient but also as a binder, and shows fine 25 miscibility with other coating resin and less adverse influence on the environment.

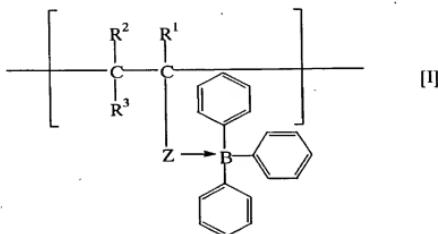
Brief Description of the Drawing

Fig. 1 shows an IR (infrared) spectrum of a polymer obtained in Example 5.

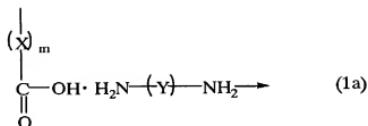
Fig. 2 shows an IR (infrared) spectrum of a polymer 30 obtained in Example 45.

Embodiment of the Invention

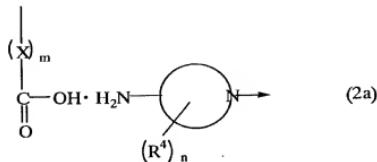
The present invention relates to a polymer containing a triphenylboron-containing constituting unit of the formula [I]:



wherein R^1 , R^2 and R^3 are the same or different and each is a hydrogen atom or alkyl group having 1 to 4 carbon atoms;
 Z is a group of the formula (1a):



or the formula (2a):



wherein, in the formulas (1a) and (2a), X is alkylene group having 1 to 18 carbon atoms, arylene group, aralkylene group, $-C(=O)-$ group, $-C(=O)-R^5-$ group, $-C(=O)-O-R^5-$ group, $-O-R^5-$ group, $-C(=O)-O-R^5-O-C(=O)-$ group or $-C(=O)-O-R^5-O-C(=O)-R^6-$ group (where R^5 and R^6 are the same or different and each is alkylene group having 1 to 18 carbon atoms or arylene group); Y is alkylene group having 2 to 18 carbon atoms, arylene group, aralkylene group or cycloalkylene group; m is 0 or 1; R^4 in the number of n are the same or different and each is halogen atom or alkyl group having 1 to 18 carbon atoms; n is an integer of 0-3; and a group of the formula (2b):



is amino-substituted, N-containing heterocycle, a composition containing the polymer and a fouling preventive containing the polymer.

The present invention is explained in detail in the following.

The alkyl group having 1 to 4 carbon atoms at R^1 , R^2 and R^3 in the formula [I] is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and the like, with preference given to methyl.

Preferable examples of each of R^1 , R^2 and R^3 include hydrogen atom and methyl.

The halogen atom at R^4 in the formula (2a) is exemplified by chlorine atom, bromine atom, fluorine atom and the like.

The alkyl group having 1 to 18 carbon atoms at R^4 is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-dodecyl, n-octadecyl and the like, with preference given to

alkyl group having 1 to 4 carbon atoms. As R⁴, hydrogen atom or alkyl group having 1 to 4 carbon atoms is preferable. As n, 0 or 1 is preferable.

The alkylene group having 1 to 18 carbon atoms at X in the formulas (1a) and (2a) is exemplified by straight or branched chain alkylene group such as methylene, ethylene, trimethylene, propylene, tetramethylene, 3-methyltetramethylene, octamethylene, dodecamethylene, octadecamethylene and the like, with preference given to alkylene group having 1 to 4 carbon atoms.

The arylene group at X in the formulas (1a) and (2a) is exemplified by o-phenylene, m-phenylene, p-phenylene, 1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference given to p-phenylene.

The aralkylene group at X in the formulas (1a) and (2a) is exemplified by -Ar-Alk- or -Alk-Ar- where Ar is arylene group and Alk is alkylene group, such as benzylene (-C₆H₄-CH₂- or -CH₂-C₆H₄-), phenethylene (-C₆H₄-C₂H₅- or -C₂H₅-C₆H₄-) and the like, with preference given to benzylene.

The alkylene group having 1 to 18 carbon atoms at R⁵ and R⁶ of -C(=O)-R⁵- group, -C(=O)-O-R⁵- group, -O-R⁵- group, -C(=O)-O-R⁵-O-C(=O)- group or -C(=O)-O-R⁵-O-C(=O)-R⁶- group for X in the formulas (1a) and (2a) is exemplified by straight or branched chain alkylene group such as methylene, ethylene, trimethylene, propylene, tetramethylene, 2-methyltetramethylene, 3-methyltetramethylene, octamethylene, dodecamethylene, octadecamethylene and the like, with preference given to alkylene group having 1 to 4 carbon atoms.

The arylene group at R⁵ and R⁶ of -C(=O)-R⁵- group, -C(=O)-O-R⁵- group, -O-R⁵- group, -C(=O)-O-R⁵-O-C(=O)- group or -C(=O)-O-R⁵-O-C(=O)-R⁶- group for X in the formulas (1a) and (2a) is exemplified by o-phenylene, m-phenylene, p-phenylene,

1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference given to p-phenylene.

5 The X in the formulas (1a) and (2a) may be void ($m=0$) or preferable alkylene group having 1 to 4 carbon atoms.

The alkylene group having 2 to 18 carbon atoms at Y in the formula (1a) is exemplified by alkylene such as ethylene, trimethylene, propylene, tetramethylene, pentamethylene, 10 hexamethylene, octamethylene, dodecamethylene, octadecamethylene and the like, with preference given to ethylene and propylene.

The arylene group at Y in the formula (1a) is exemplified by o-phenylene, m-phenylene, p-phenylene, 1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference given to p-phenylene.

The aralkylene group at Y in the formula (1a) is exemplified by -Ar-Alk- or -Alk-Ar- where Ar is arylene group 20 and Alk is alkylene group, such as benzylene (-C₆H₄-CH₂- or -CH₂-C₆H₄-), phenethylene (-C₆H₄-C₂H₅- or -C₂H₅-C₆H₄-) and the like, with preference given to benzylene.

The cycloalkylene group at Y in the formula (1a) preferably has 3-10 carbon atoms, such as cyclopropylene, 25 cyclobutylene, cyclohexylene, cyclooctylene, cyclodecylene and the like, with preference given to cyclohexylene.

The Y in the formula (1a) is preferably ethylene, propylene or p-phenylene.

The N-containing heterocycle of the amino-substituted, 30 N-containing heterocycle in the formula (2b) may be a monoheterocycle or condensed heterocycle, or saturated heterocycle or unsaturated heterocycle, or may contain sulfur atom or oxygen atom. Preferably, it is a 5 or 6-membered ring or a condensed ring containing the same, such as pyridine ring,

pyrimidine ring, pyrrole ring, pyrazole ring, pyrrolidine ring, pyrazoline ring, piperidine ring, piperazine ring, pyrazine ring, purine ring, imidazole ring, benzoimidazole ring, indole ring, indazole ring, triazole ring, carbazole ring,
 5 phenothiazine ring, phenoxazine ring, quinoline ring and the like, with preference given to pyridine ring and piperidine ring.

The alkyl group having 1 to 4 carbon atoms at R⁷ in the formula (4) is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and the like, with preference given to methyl. As R⁷, hydrogen atom and methyl are preferable.

The organic acid residue at R⁸, R⁹ and R¹⁰ in the formula (4) refers to the residue of carboxyl of organic acid after 15 eliminating hydrogen atom, wherein the organic acid is exemplified by optionally substituted saturated and unsaturated aliphatic carboxylic acid having 1 to 18 carbon atoms such as acrylic acid, methacrylic acid, propionic acid, octyl acid, versatic acid, stearic acid, isostearic acid, palmitic acid, 20 monochloroacetic acid, monofluoroacetic acid and the like; optionally substituted aromatic carboxylic acid such as benzoic acid, α -naphthoic acid, β -naphthoic acid, nitrobenzoic acid, nitronaphthalenecarboxylic acid, salicylic acid, cresotinic acid and the like; optionally substituted aromatic aliphatic 25 carboxylic acid such as 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid and the like; heterocyclecarboxylic acid such as quinolinecarboxylic acid and the like; pyruvic acid and the like.

The alkyl group having 1 to 18 carbon atoms at R⁸, R⁹ and 30 R¹⁰ in the formula (4) is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, hexyl, octyl, 2-ethylhexyl, dodecyl, octadecyl and the like.

The aryl group at R⁸, R⁹ and R¹⁰ in the formula (4) is

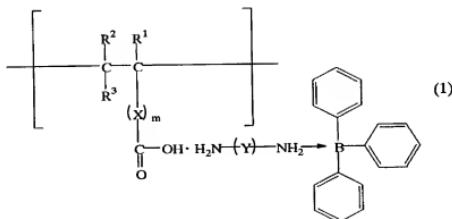
exemplified by phenyl, naphthyl and the like.

The cycloalkyl group at R^8 , R^9 and R^{10} in the formula (4) is exemplified by those having 3 to 10 carbon atoms, such as cyclopropyl, cyclohexyl, cyclooctyl, cyclodecyl and the like.

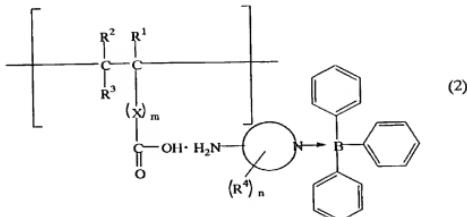
5 The metal atom at M in the formula (4) is exemplified by Cu, Zn, Fe, Ni, Co, Pb, Al, Mg and the like, with preference given to Cu, Zn and Mg.

When M is a metal atom, R^8 , R^9 and R^{10} are preferably aliphatic carboxylic acid residue having 1 to 18 carbon atoms, 10 and when M is a silicon atom, R^8 , R^9 and R^{10} are preferably alkyl group having 1 to 4 carbon atoms.

As the polymer containing triphenylboron of the present invention, there is mentioned a polymer containing a triphenylboron-containing constituting unit of the following 15 the formula (1):



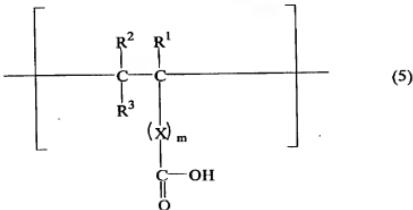
or the formula (2):



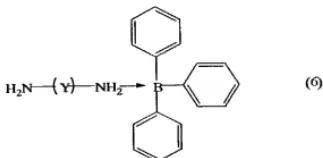
wherein each symbol in the formulas (1) and (2) is as defined above.

Polymer containing triphenylboron (1)

In the polymer containing a triphenylboron-containing constituting unit of the formula (1) (hereinafter to be also referred to as a polymer containing triphenylboron (1)) of the present invention, triphenylboron-containing constituting unit 5 of the formula (1) consists of a carboxyl group-containing constituting unit of the formula (5):



wherein each symbol is as defined above, and a diamine adduct of triphenylboron of the formula (6):



10 wherein each symbol is as defined above.

The carboxyl group-containing constituting unit of the formula (5) is exemplified by constituting units derived from carboxyl group-containing polymerizable unsaturated monomer, such as acrylic acid, crotonic acid, isocrotonic acid, 15 vinylacetic acid, methacrylic acid, 2-ethylacrylic acid, 2-n-propylacrylic acid, 2-isopropylacrylic acid, 2-n-buty lacrylic acid, 2-sec-buty lacrylic acid, 2-tert-buty lacrylic acid, 2-ethyl-2-butenoic acid, 2-n-propyl-2-butenoic acid, 2-isopropyl-2-butenoic acid, 2-n-buty-2-butenoic acid, 2-sec-buty-2- 20 butenoic acid, 2-tert-buty-2-butenoic acid, 2-pentenoic acid, 2-methyl-2-pentenoic acid, 3-methyl-2-pentenoic acid, 4-methyl-2-pentenoic acid, 2-ethyl-2-pentenoic acid, 2-n-propyl-2-

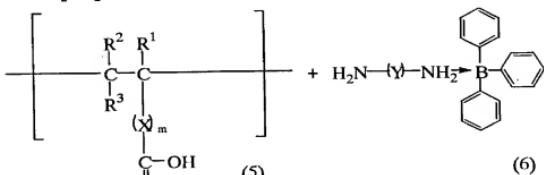
pentenoic acid, 2-isopropyl-2-pentenoic acid, 2-n-butyl-2-pentenoic acid, 2-sec-butyl-2-pentenoic acid, 2-tert-butyl-2-pentenoic acid, 3-pentenoic acid, 4-methyl-3-pentenoic acid, 2-hexenoic acid, 2-methyl-2-hexenoic acid, 2-ethyl-2-hexenoic acid, 2-n-propyl-2-hexenoic acid, 2-isopropyl-2-hexenoic acid, 2-n-butyl-2-hexenoic acid, 2-sec-butyl-2-hexenoic acid, 2-tert-butyl-2-hexenoic acid, 3-hexenoic acid, 4-hexenoic acid, 5-hexenoic acid, 2-heptenoic acid, 2-methyl-2-heptenoic acid, 2-ethyl-2-heptenoic acid, 2-n-propyl-2-heptenoic acid, 2-isopropyl-2-heptenoic acid, 2-n-butyl-2-heptenoic acid, 2-sec-butyl-2-heptenoic acid, 2-tert-butyl-2-heptenoic acid, 3-heptenoic acid, 4-heptenoic acid, 5-heptenoic acid, 6-heptenoic acid, 4-methyl-2-hexenoic acid, 5-methyl-2-hexenoic acid, 4,4-dimethyl-2-pentenoic acid, 2,4-dimethyl-2-pentenoic acid, 2,4-dimethyl-2-hexenoic acid, 2,5-dimethyl-2-hexenoic acid, 2,4,4-trimethyl-2-pentenoic acid, 3-methyl-2-butenoic acid, 2,3-dimethyl-2-butenoic acid, 3-methyl-2-pentenoic acid, 2,3-dimethyl-2-pentenoic acid, 3-methyl-2-hexenoic acid, 2,3-dimethyl-2-hexenoic acid, 3,4-dimethyl-2-pentenoic acid, 2,3,4-trimethyl-2-pentenoic acid, 3-methyl-2-heptenoic acid, 2,3-dimethyl-2-heptenoic acid, 3,4-dimethyl-2-hexenoic acid, 2,3,4-trimethyl-2-hexenoic acid, 3,5-dimethyl-2-hexenoic acid, 2,3,5-trimethyl-2-hexenoic acid, 3,4,4-trimethyl-2-pentenoic acid, 2,3,4,4-tetramethyl-2-pentenoic acid, 7-octenoic acid, 11-dodecanoic acid, 15-hexadecenoic acid, 17-octadecenoic acid, 2-methyl-3-butenoic acid, 2-methyl-4-pentenoic acid, 2-methyl-5-hexenoic acid, 2-methyl-6-heptenoic acid, 2-methyl-7-octenoic acid, 2-methyl-11-dodecanoic acid, 2-methyl-15-hexadecenoic acid, 2-methyl-17-octadecenoic acid, 4-vinylbenzoic acid, 4-(1-propenyl)benzoic acid, 4-(isopropenyl)benzoic acid, 4-(1-methyl-1-propenyl)benzoic acid, 4-vinylphenylacetic acid, 4-(1-propenyl)phenylacetic acid, 4-(isopropenyl)phenylacetic acid, 4-(1-methyl-1-propenyl)phenylacetic acid, 4-(2-methyl-1-propenyl)phenylacetic

acid, 2-oxo-3-butenoic acid, 3-oxo-4-pentenoic acid, 4-oxo-5-hexenoic acid, carboxymethyl acrylate, 2-carboxyethyl acrylate, 3-carboxypropyl acrylate, 4-carboxybutyl acrylate, 5-carboxypentyl acrylate, 6-carboxyhexyl acrylate, 7-carboxyheptyl acrylate, 8-carboxyoctyl acrylate, 12-carboxydodecyl acrylate, 18-carboxyoctadecyl acrylate, o-carboxyphenyl acrylate, m-carboxyphenyl acrylate, p-carboxyphenyl acrylate, 2-vinylxyloacetic acid, 3-vinylxylopropionic acid, monoacryloyloxyethyl oxalate, mono-3-acryloyloxypropyl oxalate, monoacryloyloxyethyl malonate, mono-3-acryloyloxypropyl malonate and the like, with preference given to constituting unit derived from acrylic acid and methacrylic acid. These constituting units may be contained solely or in combination of two or more kinds thereof in a polymer.

The diamine of the formula (7) below of the diamine adduct of triphenylboron expressed by the formula (6) is exemplified by alkylenediamines having 2 to 18 carbon atoms, such as ethylenediamine, propylenediamine, trimethylenediamine, tetramethylenediamine, 1,3-diaminobutane, 2,3-diaminobutane, pentamethylenediamine, 2,4-diaminopentane, hexamethylenediamine, octamethylenediamine, dodecamethylenediamine, octadecamethylenediamine and the like; arylenediamines such as phenylenediamines (e.g., m-phenylenediamine, p-phenylenediamine etc.), naphthylenediamines (e.g., 1,4-diaminonaphthalene, 1,5-diaminonaphthalene etc.), and the like; aminoaralkylamines such as aminobenzylamines (e.g., 3-aminobenzylamine, 4-aminobenzylamine etc.), aminophenethylamines (e.g., 3-aminophenethylamine, 4-aminophenethylamine etc.), and the like; diaminocycloalkanes such as 1,3-diaminocyclohexane, 1,4-diaminocyclohexane and the like; and the like, with preference given to ethylenediamine, propylenediamine and p-phenylenediamine.

The polymer containing triphenylboron (1) of the present invention can be synthesized by, for example, the following method.

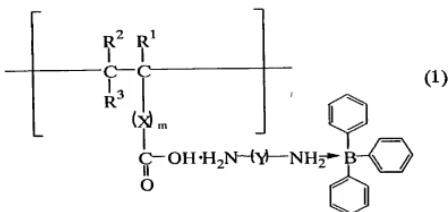
A polymer containing



as a repeating unit



A polymer containing



as a repeating unit

wherein each symbol is as defined above.

That is, the polymer containing triphenylboron (1) can be obtained by adding dropwise a diamine adduct of triphenylboron of the formula (6) or a solution thereof to a solution of polymer containing a carboxyl group-containing constituting unit of the formula (5) (hereinafter this polymer is sometimes to be referred to as a carboxyl group-containing polymer) to allow reaction and removing the solvent by distilling away under reduced pressure.

In the above-mentioned method, the diamine adduct of triphenylboron of the formula (6) is preferably used in an

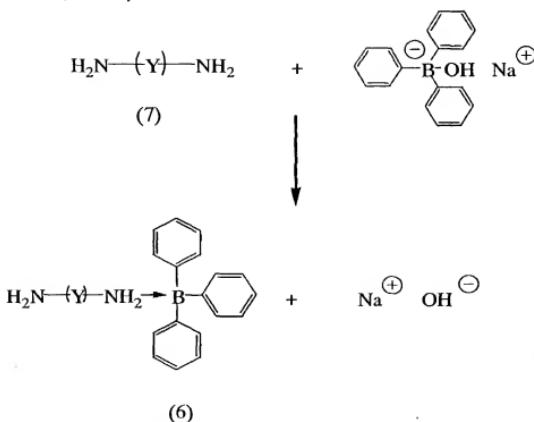
amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to the carboxyl group of the polymer containing the carboxyl group-containing constituting unit of the formula (5). When this amount of use is less than 0.1 equivalent, 5 adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, when it exceeds 3.0 equivalents, unreacted diamine adduct of triphenylboron remains excessively and the prevention of adhesion is no longer efficient even if increase in addition 10 efficiency is taken into consideration.

The solvent to be used in the above-mentioned method is not particularly limited as long as it does not affect the reaction adversely. For example, xylene, n-butanol, toluene, chloroform, propylene glycol monomethyl ether and the like are 15 mentioned, which may be used alone or in combination of two or more kinds thereof.

The temperature of reaction between diamine adduct of triphenylboron of the formula (6) and a polymer containing a carboxyl group-containing constituting unit of the formula (5) 20 is generally room temperature, and can be changed to 100°C as necessary. The reaction time is generally from about 30 minutes to 24 hours.

The polymer containing a carboxyl group-containing constituting unit of the formula (5) is obtained by 25 polymerizing a polymerizable unsaturated monomer including the above-mentioned carboxyl group-containing polymerizable unsaturated monomer by a conventionally-known method.

The diamine adduct of triphenylboron of the formula (6) can be synthesized by, for example, the method shown by the 30 following formulas.

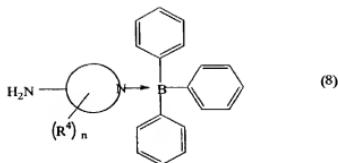


wherein each symbol is as defined above

That is, the diamine adduct of triphenylboron of the formula (6) can be obtained by adding dropwise diamine of the formula (7) to an aqueous solution of a sodium hydroxide adduct of triphenylboron, and when the objective substance precipitated as an insoluble material, by collecting the insoluble material by filtration, washing with water and drying, and when the objective substance is dissolved, by partitioning and removing the solvent by distilling away under reduced pressure.

Polymer containing triphenylboron (2)

The triphenylboron-containing constituting unit of the formula (2) of the polymer containing a triphenylboron-containing constituting unit of the formula (2) (hereinafter to be also referred to as a polymer containing triphenylboron (2)) of the present invention consists of the carboxyl group-containing constituting unit of the above-mentioned formula (5), and an N-containing heterocyclic adduct of triphenylboron of the formula (8):

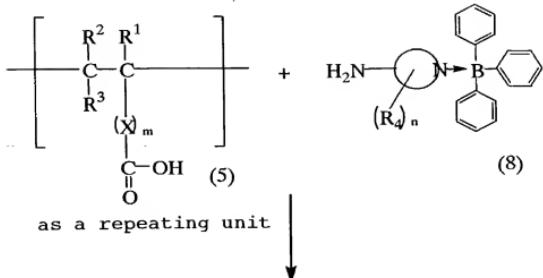


wherein each symbol is as defined above, which is an adduct of triphenylboron and an amino group-substituted, N-containing heterocycle of the formula (9) to be mentioned below.

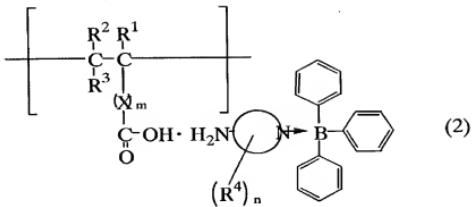
5 The amino group-substituted, N-containing heterocycle of the N-containing heterocyclic adduct of triphenylboron of the formula (8) is, for example, 3-aminopyridine, 4-aminopyridine, 4-aminopyrimidine, 5-aminopyrimidine, 3-aminopyrazole, 4-aminopyrazole, 4-aminoimidazole, 4-aminoindazole, 5-
 10 aminoindazole, 4-aminoindole, 5-aminoindole, 4-aminobenzoimidazole, 3-aminopyrrolidine, 3-aminopiperidine, 4-aminopiperidine, 3-aminoquinoline, 5-aminoquinoline, 1-aminopiperazine, aminopyrazine, 2-aminopurine, 3-aminopyrrole, 3-aminopyrazoline, 3-amino-1,2,4-triazole, 4-amino-1,2,4-
 15 triazole, 4-aminocarbazole, 4-aminophenothiazine, 4-aminophenoxazine and the like, with preference given to 4-aminopyridine and 4-aminopiperidine.

15 The polymer containing triphenylboron (2) of the present invention can be synthesized by, for example, the following
 20 method.

A polymer containing



a polymer containing



as a repeating unit

wherein each symbol is as defined above.

That is, the polymer containing triphenylboron (2) can be obtained by adding dropwise an N-containing heterocyclic adduct of triphenylboron of the formula (8) or a solution thereof to a solution of polymer containing a carboxyl group-containing constituting unit of the formula (5) to allow reaction and removing the solvent by distilling away under reduced pressure.

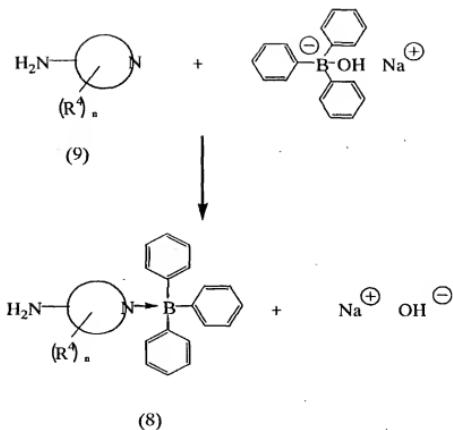
10 In the above-mentioned method, the N-containing heterocyclic adduct of triphenylboron of the formula (8) is preferably used in an amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to the carboxyl group of the polymer containing the carboxyl group-containing constituting

unit of the formula (5). When this amount of use is less than 0.1 equivalent, adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, when it exceeds 3.0 equivalents, 5 unreacted N-containing heterocyclic adduct of triphenylboron remains excessively and the prevention of adhesion is no longer efficient even if increase in addition efficiency is taken into consideration.

The solvent to be used in the above-mentioned method is 10 not particularly limited as long as it does not affect the reaction adversely. For example, xylene, toluene, chloroform, n-butanol, propylene glycol monomethyl ether and the like are mentioned, which may be used alone or in combination of two or more kinds thereof.

15 The temperature of reaction between N-containing heterocyclic adduct of triphenylboron of the formula (8) and a polymer having a carboxyl group-containing constituting unit of the formula (5) is generally room temperature, and can be changed to 100°C as necessary. The reaction time is generally 20 from about 30 minutes to 24 hours.

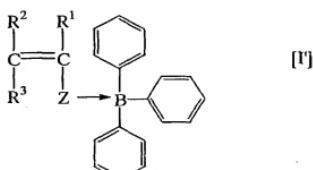
The N-containing heterocyclic adduct of triphenylboron of the formula (8) can be synthesized by, for example, the following method:



wherein each symbol is as defined above.

That is, N-containing heterocyclic adduct of triphenylboron of the formula (8) is obtained by adding the amino-substituted, N-containing heterocycle of the formula (9) to an aqueous solution of a sodium hydroxide adduct of triphenylboron, and washing with water and drying the precipitated insoluble material.

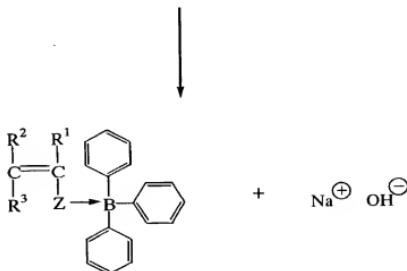
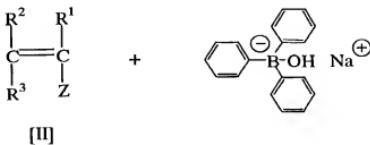
The above-mentioned polymers containing triphenylboron (1) and (2) can be produced by the following method, besides the above-mentioned production method. That is, the above-mentioned polymers containing triphenylboron (1) and (2) can be synthesized by homopolymerization of a triphenylboron-containing vinyl monomer of the formula [I']:



wherein each symbol is as defined above, or copolymerization of this monomer and a different polymerizable unsaturated monomer.

The above-mentioned triphenylboron-containing vinyl monomer of the formula [I'] can be synthesized by the following 5 three methods.

Method 1:

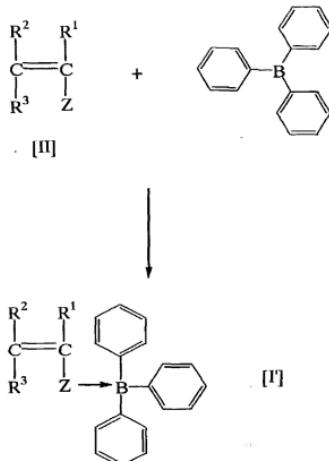


[I']

wherein each symbol is as defined above.

The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by adding dropwise a solution 10 containing vinyl compound of the above-mentioned formula [II] to an aqueous solution of sodium hydroxide adduct of triphenylboron, and when the objective substance precipitated as an insoluble material, by collecting the insoluble material by filtration, washing with water and drying, and when the 15 objective substance is dissolved, by partitioning and removing the solvent by distilling away under reduced pressure.

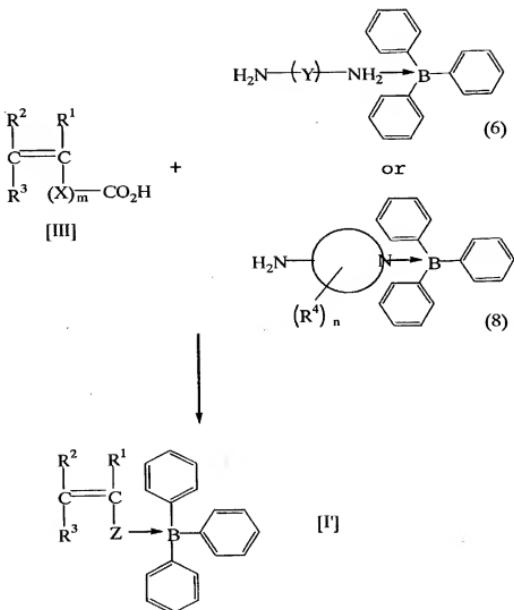
Method 2:



wherein each symbol is as defined above.

The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by reacting the vinyl compound of the above-mentioned formula [II] and triphenylboron in an organic solvent such as toluene, xylene, chloroform, dimethylsulfoxide, n-butanol, propylene glycol monomethyl ether and the like.

Method 3:



wherein each symbol is as defined above.

The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by reacting the vinyl compound of the above-mentioned formula [III] and a diamine adduct of triphenylboron of the formula (6) or N-containing heterocyclic adduct of triphenylboron of the formula (8).

The triphenylboron to be used in the present invention may be commercially available or can be produced by reacting boron trifluoride and phenylmagnesium bromide.

The polymers containing triphenylboron (1) and (2) of the present invention have a weight average molecular weight of preferably 1,000-1,000,000, particularly preferably 3,000-

500,000. When the molecular weight is less than 1,000, the coating film formed becomes brittle, and conversely, when it exceeds 1,000,000, the polymer solution has a higher viscosity, which unpreferably makes its handling difficult.

5 The content of the triphenylboron-containing constituting unit of the formula (1) or (2) in the polymer containing triphenylboron (1) and (2) of the present invention is each preferably not less than 1.0 wt%, more preferably 5-95 wt%, particularly preferably 5-70 wt%. When the content is 10 less than 1.0 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient.

15 The content of the triphenylboron in the polymer containing triphenylboron (1) and (2) of the present invention is each preferably not less than 0.5 wt%, more preferably 3-60 wt%, particularly preferably 3-45 wt%. When the content is less than 0.5 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient.

20 The polymers containing triphenylboron (1) and (2) of the present invention may contain a constituting unit derived from a polymerizable unsaturated monomer other than the triphenylboron-containing constituting unit of the formula (1) or (2). By containing such constituting unit, the triphenylboron content of the polymers containing triphenylboron (1) and (2) can be adjusted. Therefore, a 25 polymer containing a carboxyl group-containing constituting unit of the formula (5) may be a homopolymer or a copolymer. The copolymer is obtained by copolymerizing the aforementioned carboxyl group-containing polymerizable unsaturated monomer and a polymerizable unsaturated monomer other than the carboxyl 30 group-containing polymerizable unsaturated monomer.

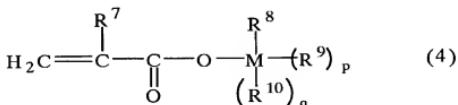
The constituting unit derived from a polymerizable unsaturated monomer other than the triphenylboron-containing constituting unit of the formula (1) or (2) is, for example, a constituting unit derived from a polymerizable unsaturated

monomer without boron. Such polymerizable unsaturated monomer is, for example, vinyl hydrocarbons such as ethylene, propylene, butadiene, isoprene, styrene, α -methylstyrene, vinyltoluene, divinylbenzene, indene and the like; acrylonitriles such as 5 acrylonitrile, methacrylonitrile and the like; unsaturated carboxylic acids such as acrylic acid, crotonic acid, isocrotonic acid, methacrylic acid, vinylacetic acid, vinylpropionic acid, vinylbutyric acid, p-vinylbenzoic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, 10 mesaconic acid and the like; unsaturated carboxylic anhydrides such as maleic anhydride, itaconic anhydride, citraconic anhydride and the like; vinyl heterocyclic compounds such as 2-vinylpyridine, 4-vinylpyridine, N-vinyl-2-pyrrolidone, vinylcarbazole and the like; vinyl esters such as vinyl formate, 15 vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl benzoate and the like; halogenated vinyls such as vinyl chloride, vinylidene chloride and the like; vinylamines; allylamines; vinyl alcohols; allyl alcohols; vinyl ketones such as methyl vinyl ketone, phenyl 20 vinyl ketone and the like; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, lauryl vinyl ether, phenyl vinyl ether, benzyl vinyl ether and the like; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl 25 acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, cetyl acrylate, stearyl acrylate, vinyl acrylate, benzyl acrylate, phenyl acrylate, isobornyl acrylate, cyclohexyl acrylate, glycidyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxybutyl acrylate, 4- 30 hydroxybutyl acrylate, glycerol acrylate, butylaminoethyl acrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminopropyl acrylate, dimethylaminobutyl acrylate, dibutylaminoethyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, phenoxyethyl acrylate, 2-(2-

ethylhexyloxy)ethyl acrylate, 1-methyl-2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 3-methyl-3-methoxybutyl acrylate, o-methoxyphenyl acrylate, m-methoxyphenyl acrylate, p-methoxyphenyl acrylate, o-methoxyphenylethyl acrylate, m-methoxyphenylethyl acrylate, p-methoxyphenylethyl acrylate and the like; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, vinyl methacrylate, benzyl methacrylate, phenyl methacrylate, isobornyl methacrylate, cyclohexyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxybutyl methacrylate, 4-hydroxybutyl methacrylate, glycerol methacrylate, butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, dimethylaminobutyl methacrylate, dibutylaminoethyl methacrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, phenoxyethyl methacrylate, 2-(2-ethylhexyloxy)ethyl methacrylate, 1-methyl-2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate, 3-methyl-3-methoxybutyl methacrylate, o-methoxyphenyl methacrylate, m-methoxyphenyl methacrylate, p-methoxyphenyl methacrylate, o-methoxyphenylethyl methacrylate, m-methoxyphenylethyl methacrylate and the like; acrylic acid amides such as acrylamide, dimethylaminoethylacrylamide, dimethylaminopropylacrylamide and the like; methacrylic acid amides such as methacrylamide, dimethylaminoethylmethacrylamide, dimethylaminopropylmethacrylamide and the like; cyanoacrylic acid esters; acrolein, cumarone, indene, tetrafluoroethylene, vinyl formal, vinyl formamide and the like, with preference given to ethylene and esters derived from acrylic acid or

methacrylic acid such as methyl methacrylate, 2-ethylhexyl acrylate, methyl acrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate and the like.

In addition, a polymerizable unsaturated monomer of the formula (4):



wherein R⁷ is hydrogen atom or alkyl group having 1 to 4 carbon atoms; M is metal atom or silicon atom; when M is metal atom, R⁸, R⁹ and R¹⁰ are the same or different and each is organic acid residue, when M is silicon atom, R⁸, R⁹ and R¹⁰ are the same or different and each is alkyl group having 1 to 18 carbon atoms, aryl group or cycloalkyl group; p and q are both 0 when M is divalent metal atom, p is 1 and q is 0 when M is a trivalent metal atom, and both are 1 when M is quatervalent metal atom, is also mentioned. In the above-mentioned formula (4), (meth)acrylic acid metal salt and silyl (meth)acrylate are preferable, and as M, a metal atom such as zinc, copper and magnesium, and silicon atom are preferable.

Examples of the polymerizable unsaturated monomer include the following.

25 zinc salts of acrylic acid such as zinc acrylate, zinc acrylate benzoate, zinc acrylate propionate, zinc acrylate octylate, zinc acrylate versatate, zinc acrylate stearate, zinc acrylate isostearate, zinc acrylate palmitate, zinc acrylate cresotinate, zinc acrylate α -naphthoate, zinc acrylate β -naphthoate, zinc acrylate monochloroacetate, zinc acrylate monofluoroacetate, zinc acrylate 2,4-dichlorophenoxyacetate, zinc acrylate 2,4,5-trichlorophenoxyacetate, zinc acrylate 30 quinolinecarboxylate, zinc acrylate nitrobenzoate, zinc

acrylate nitronaphthalenecarboxylate, zinc acrylate pyruvate and the like;

zinc salts of methacrylic acid such as zinc methacrylate, zinc methacrylate benzoate, zinc methacrylate propionate, zinc methacrylate octylate, zinc methacrylate versatate, zinc methacrylate stearate, zinc methacrylate isostearate, zinc methacrylate palmitate, zinc methacrylate cresotinate, zinc methacrylate α -naphthoate, zinc methacrylate β -naphthoate, zinc methacrylate monochloroacetate, zinc methacrylate monofluoroacetate, zinc methacrylate 2,4-dichlorophenoxyacetate, zinc methacrylate 2,4,5-trichlorophenoxyacetate, zinc methacrylate quinolinecarboxylate, zinc methacrylate nitrobenzoate, zinc methacrylate nitronaphthalenecarboxylate, zinc methacrylate pyruvate and the like;

15 copper salts of acrylic acid such as copper acrylate, copper acrylate benzoate, copper acrylate propionate, copper acrylate octylate, copper acrylate versatate, copper acrylate stearate, copper acrylate isostearate, copper acrylate palmitate, copper acrylate cresotinate, copper acrylate α -naphthoate, copper acrylate β -naphthoate, copper acrylate monochloroacetate, copper acrylate monofluoroacetate, copper acrylate 2,4,5-trichlorophenoxyacetate, copper acrylate quinolinecarboxylate, copper acrylate nitrobenzoate, copper acrylate nitronaphthalenecarboxylate, copper acrylate pyruvate and the like;

25 copper salts of methacrylic acid such as copper methacrylate, copper methacrylate benzoate, copper methacrylate propionate, copper methacrylate octylate, copper methacrylate versatate, copper methacrylate stearate, copper methacrylate isostearate, copper methacrylate palmitate, copper methacrylate cresotinate, copper methacrylate α -naphthoate, copper methacrylate β -naphthoate, copper methacrylate monochloroacetate, copper methacrylate monofluoroacetate, copper methacrylate 2,4-

dichlorophenoxyacetate, copper methacrylate 2,4,5-
 trichlorophenoxyacetate, copper methacrylate
 quinolinecarboxylate, copper methacrylate nitrobenzoate, copper
 methacrylate nitronaphthalenecarboxylate, copper methacrylate
 5 pyruvate and the like;
 magnesium salts of acrylic acid such as magnesium
 acrylate, magnesium acrylate benzoate, magnesium acrylate
 propionate, magnesium acrylate octylate, magnesium acrylate
 versatate, magnesium acrylate stearate, magnesium acrylate
 10 isostearate, magnesium acrylate palmitate, magnesium acrylate
 cresotinate, magnesium acrylate α -naphthoate, magnesium
 acrylate β -naphthoate, magnesium acrylate monochloroacetate,
 magnesium acrylate monofluoroacetate, magnesium acrylate 2,4-
 dichlorophenoxyacetate, magnesium acrylate 2,4,5-
 15 trichlorophenoxyacetate, magnesium acrylate
 quinolinecarboxylate, magnesium acrylate nitrobenzoate,
 magnesium acrylate nitronaphthalenecarboxylate, magnesium
 acrylate pyruvate and the like;
 magnesium salts of methacrylic acid such as magnesium
 20 methacrylate, magnesium methacrylate benzoate, magnesium
 methacrylate propionate, magnesium methacrylate octylate,
 magnesium methacrylate versatate, magnesium methacrylate
 stearate, magnesium methacrylate isostearate, magnesium
 methacrylate palmitate, magnesium methacrylate cresotinate,
 25 magnesium methacrylate α -naphthoate, magnesium methacrylate β -
 naphthoate, magnesium methacrylate monochloroacetate, magnesium
 methacrylate monofluoroacetate, magnesium methacrylate 2,4-
 dichlorophenoxyacetate, magnesium methacrylate 2,4,5-
 trichlorophenoxyacetate, magnesium methacrylate
 30 quinolinecarboxylate, magnesium methacrylate nitrobenzoate,
 magnesium methacrylate nitronaphthalenecarboxylate, magnesium
 methacrylate pyruvate and the like;
 silyl acrylates such as trimethylsilyl acrylate,
 triethylsilyl acrylate, tri-n-propylsilyl acrylate,

triisopropylsilyl acrylate, tri-n-butylsilyl acrylate,
 triisobutylsilyl acrylate, triphenylsilyl acrylate,
 dimethylbutylsilyl acrylate, dimethylhexylsilyl acrylate,
 dimethyloctylsilyl acrylate, dimethylcyclohexylsilyl acrylate,
 5 dimethylphenylsilyl acrylate, dibutylphenylsilyl acrylate,
 methyldibutylsilyl acrylate, ethyldibutylsilyl acrylate,
 dibutylcyclohexylsilyl acrylate, dibutylphenylsilyl acrylate
 and the like;

10 silyl methacrylates such as trimethylsilyl methacrylate,
 triethylsilyl methacrylate, tri-n-propylsilyl methacrylate,
 triisopropylsilyl methacrylate, tri-n-butylsilyl methacrylate,
 triisobutylsilyl methacrylate, triphenylsilyl methacrylate,
 dimethylbutylsilyl methacrylate, dimethylhexylsilyl
 methacrylate, dimethyloctylsilyl methacrylate,
 15 dimethylcyclohexylsilyl methacrylate, dimethylphenylsilyl
 methacrylate, dibutylphenylsilyl methacrylate,
 methyldibutylsilyl methacrylate, ethyldibutylsilyl methacrylate,
 dibutylcyclohexylsilyl methacrylate, dibutylphenylsilyl
 methacrylate and the like.

20 Of the above-mentioned examples, preferred are zinc
 salts of (meth)acrylic acid, copper salts of (meth)acrylic acid
 and magnesium salts of (meth)acrylic acid, particularly
 preferred are zinc salts of (meth)acrylic acid.

The content of the above-mentioned constituting unit
 25 derived from a polymerizable unsaturated monomer other than the
 triphenylboron-containing constituting unit of the formula (1)
 or (2) is preferably 0-99 wt%, more preferably 5-95 wt%, in the
 polymer containing triphenylboron (1) or (2) of the present
 invention. When the content exceeds 99 wt%, the adhesion-
 30 preventive effect against aquatic fouling organisms
 unpreferably becomes insufficient.

The above-mentioned polymerizable unsaturated monomer is
 introduced during synthesis of a polymer containing a carboxyl
 group-containing constituting unit of the formula (5) or during

polymerization of a triphenylboron-containing vinyl monomer of the formula [I']. The above-mentioned polymerizable unsaturated monomer may be used alone or in combination of two or more kinds thereof.

5 The polymers containing triphenylboron (1) and (2) of the present invention can be prepared into a fouling preventive such as a fishnet antifouling agent, an underwater antifouling coating (e.g., ship bottom antifouling coating) and the like by a conventional method such as the following methods.

10 A. Fishnet antifouling agent

The fishnet antifouling agent of the present invention shows low toxicity, is highly safe and shows a superior adhesion-preventive effect against coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, Serpula etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms for a long time.

The fishnet antifouling agent of the present invention is prepared by dispersing or dissolving a polymer containing 20 triphenylboron (1) or (2) in an organic solvent. The content of the polymer containing triphenylboron (1) or (2) in the fishnet antifouling agent of the present invention can be changed according to the environment of application, which is preferably 1-50 wt%, more preferably 3-25 wt%. When the 25 content is less than 1 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient. Conversely, when it exceeds 50 wt%, the fishnet antifouling agent has a higher viscosity, which unpreferably makes its handling difficult.

30 The organic solvent to be used for the fishnet antifouling agent of the present invention includes organic solvent of aromatic compound, organic solvent of ketone compound, organic solvent of aliphatic compound and the like. Specific examples include xylene, toluene, pseudocumene,

diethylbenzene, triethylbenzene, mesitylene, solvent naphtha, butanol, isopropanol, methyl isobutyl ketone, hexane, propylene glycol monomethyl ether and the like. These solvents may be used alone or in combination of two or more kinds thereof.

5 Where necessary, various resins such as acrylic resin, synthetic rubber, rosin resin, silicone resin, polybutene resin, rubber chloride resin, vinyl chloride resin, alkyd resin, cumarone resin, ethylene-vinyl acetate resin, epoxide resin and the like may be added. These resins may be used alone or in
10 combination of two or more kinds thereof.

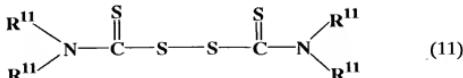
When the polymer containing triphenylboron (1) or (2) of the present invention is used as a fishnet antifouling agent, a superior adhesion-preventive effect against aquatic fouling organisms can be achieved even by this polymer alone, but
15 addition of silicone oil, elution regulator, or an antifouling component other than a polymer containing triphenylboron (1) or (2) and the like allows exhibition of a more superior adhesion-preventive effect.

The silicone oil to be used for the fishnet antifouling
20 agent of the present invention is, for example, dimethylsilicone oil, methyl hydrosilicone oil, (higher) fatty acid modified silicone oil, alkyl modified silicone oil, amino modified silicone oil, epoxy modified silicone oil, polyether modified silicone oil, methylphenylsilicone oil and the like,
25 with preference given to polyether modified silicone oil, higher fatty acid modified silicone oil and the like. These may be used alone or in combination of two or more kinds thereof. While the content of these silicone oils can be optionally varied according to the environment of application,
30 it is preferably 0.1-50 wt%, more preferably 0.5-25 wt%, in a fishnet antifouling agent. When the content is less than 0.1 wt%, an effect afforded by concurrent use is not expected, and when it exceeds 50 wt% conversely, it unpreferably degrades property of a coating film.

The antifouling component other than a polymer containing triphenylboron (1) or (2) to be used for the fishnet antifouling agent of the present invention is exemplified by known antifouling components, such as 1,3-

- 5 dicyanotetrachlorobenzene, 2-(thiocyanomethylthio)benzothiazole, bis(2-pyridylthio-1-oxide)zinc, bis(2-pyridylthio-1-oxide)copper, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, cuprous oxide, copper thiocyanate (CuSCN), N,N-dimethyldichlorophenyl urea, 4,5-dichloro-2-n-
- 10 octyl-3-isothiazolone, N-(fluorodichloromethylthio)phthalimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, zinc dimethyldithiocarbamate, bis(dimethyldithiocarbamoyl)zinc ethylene bisdithiocarbamate, pyridine-triphenylboron, triphenylboron-alkyl(3-30 carbon
- 15 atoms)amine (e.g., triphenylboron-n-octadecylamine, triphenylboron-n-hexadecylamine, triphenylboron-n-octylamine etc.), triphenylboron-rosin amine, copper rhodanide, copper hydroxide, copper naphthenate, manganese ethylene bisdithiocarbamate, zinc ethylene bisdithiocarbamate, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfide, 3-iodo-2-propynylbutylcarbamate, diiodomethylparatolylsulfane, 2-(4-thiazolyl)-benzoimidazole and the like, and antifouling compounds of other non-tin group.

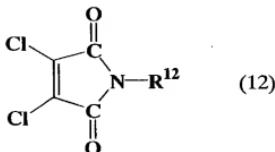
There are also mentioned tetraalkyl thiuram disulfides 25 of the formula (11):



wherein each R¹¹ is the same or different is alkyl group having 1 to 4 carbon atoms. The alkyl group having 1 to 4 carbon atoms at R¹¹ in the formula (11) is exemplified by straight or 30 branched chain alkyl such as methyl, ethyl, n-propyl, isopropyl, butyl and the like, with preference given to ethyl and butyl.

Examples of tetraalkyl thiuram disulfides of the formula (11) include tetramethyl thiuram disulfide, tetraethyl thiuram disulfide, tetraisopropyl thiuram disulfide, tetra-n-butyl thiuram disulfide and the like.

5 There are also mentioned 2,3-dichloromaleimides of the formula (12):



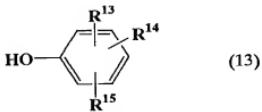
wherein R¹² is hydrogen atom, alkyl group, halogen-substituted alkyl group, cycloalkyl group, phenyl group, alkyl-substituted phenyl group, halogen-substituted phenyl group, benzyl group, 10 alkyl-substituted benzyl group or halogen-substituted benzyl group.

The alkyl group at R¹² of the formula (12) is, for example, straight or branched chain alkyl having 1 to 18 carbon atoms such as methyl, ethyl, isopropyl, n-butyl, t-butyl, octyl, 15 dodecyl, tetradecyl, hexadecyl, octadecyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like. The alkyl-substituted phenyl group is exemplified by 20 dimethylphenyl, diethylphenyl, trimethylphenyl, methylethylphenyl and the like. The halogen-substituted phenyl group is exemplified by dichlorophenyl and the like. The alkyl-substituted benzyl group is exemplified by methylbenzyl, dimethylbenzyl, diethylbenzyl, α -methylbenzyl and the like. 25 The halogen-substituted benzyl group is exemplified by chlorobenzyl, dichlorobenzyl and the like. As R¹², ethyl, butyl, diethylphenyl, methylethylphenyl, benzyl are preferable.

Specific examples of 2,3-dichloromaleimides of the formula (12) include 2,3-dichloro-N-ethylmaleimide, 2,3-

dichloro-N-isopropylmaleimide, 2,3-dichloro-N-n-butylmaleimide, 2,3-dichloro-N-tert-butylmaleimide, 2,3-dichloro-N-n-octylmaleimide, 2,3-dichloro-N-cyclohexylmaleimide, 2,3-dichloro-N-benzylmaleimide, 2,3-dichloro-N-(2-chlorobenzyl)maleimide, 2,3-dichloro-N-(4-chlorobenzyl)maleimide, 2,3-dichloro-N-(2-methylbenzyl)maleimide, 2,3-dichloro-N-(2,4-dimethylbenzyl)maleimide, 2,3-dichloro-N-(3,4-dimethylbenzyl)maleimide, 2,3-dichloro-N- α -methylbenzylmaleimide, 2,3-dichloro-N-(2,4-dichlorobenzyl)maleimide, 2,3-dichloro-N-(2-ethyl-6-methylphenyl)maleimide, 2,3-dichloro-N-(2,6-dimethylphenyl)maleimide, 2,3-dichloro-N-(2,6-diethylphenyl)maleimide, 2,3-dichloro-N-(2,4-diethylphenyl)maleimide, 2,3-dichloro-N-(2,4,6-trimethylphenyl)maleimide and the like.

There are also mentioned phenols of the formula (13):



wherein R¹³, R¹⁴ and R¹⁵ are the same or different and each is hydrogen atom, alkyl group, halogen-substituted alkyl group, 20 cycloalkyl group, phenyl group, halogen atom, alkoxy group, carboxyl group, alkenyl group or aralkyl group.

In the formula (13), the alkyl group at R¹³, R¹⁴ and R¹⁵ is exemplified by straight or branched chain alkyl having 1 to 9 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, nonyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like. The halogen atom is exemplified by fluorine atom, chlorine atom, bromine atom and 30 iodine atom. The alkoxy group is exemplified by straight or

branched chain alkoxy having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and the like. The alkenyl group is exemplified by straight or branched chain alkenyl having 2 to 4 carbon atoms such as vinyl, allyl, isopropenyl and the like.

5 The aralkyl group is exemplified by aralkyl having 7 to 9 carbon atoms such as benzyl, cumyl and the like. As R¹³, R¹⁴ and R¹⁵, hydrogen atom, fluorine atom, chlorine atom, methyl, ethyl, t-butyl, nonyl and vinyl are preferable.

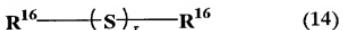
Specific examples of phenols of the formula (13) include
 10 nonylphenol, cumylphenol, 4,6-ditert-butyl-m-cresol, 1-cyclohexyl-5-methylphenol, 2,6-ditert-butyl-p-cresol, 2-phenylphenol, 2-butyl-6-ethyl-4-isopropylphenol, cyclohexyl-5-methylphenol, 2-bromo-6-chloro-4-dichloromethylphenol, 2-fluoro-4-iodo-3-trichloroethylphenol, 3-hydroxy-5-
 15 methoxybenzoic acid, 4-ethoxy-2-vinylphenol and the like.

Preferred antifouling component mentioned above other than the polymer containing triphenylboron (1) or (2) includes
 20 bis(2-pyridylthio-1-oxide)zinc, bis(2-pyridylthio-1-oxide)copper, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, cuprous oxide, copper thiocyanate (CuSCN), N,N-dimethyldichlorophenyl urea, 4,5-dichloro-2-n-octyl-3-isothiazolone, N-(fluorodichloromethylthio)phthalimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, zinc dimethyldithiocarbamate,
 25 bis(dimethyldithiocarbamoyl)zinc ethylene bisdithiocarbamate, pyridine-triphenylboron, triphenylboron-alkyl(3-30 carbon atoms)amine (e.g., triphenylboron-n-octadecylamine, triphenylboron-n-hexadecylamine, triphenylboron-n-octylamine and the like), triphenylboron-rosin amine, copper rhodanide and
 30 tetraethyl thiuram disulfide.

The above-mentioned antifouling component other than the polymer containing triphenylboron (1) or (2) may be used alone or in combination of two or more kinds thereof. The weight ratio of the above-mentioned antifouling component other than

the polymer containing triphenylboron (1) or (2) to the polymer containing triphenylboron (1) or (2) of the present invention can be optionally changed according to the environment of application, which is preferably 1:50-50:1, more preferably 5 1:25-25:1, particularly preferably 1:10-10:1. When the content of the above-mentioned antifouling component is greater than the above-mentioned range, the property of a coating film is degraded and when it is smaller conversely, an effect afforded by concurrent use is not expected.

10 The elution regulator to be used for the fishnet antifouling agent of the present invention is exemplified by dialkyl polysulfides of the formula (14):



15 wherein each \mathbf{R}^{16} is the same or different and is alkyl group having 1 to 20 carbon atoms and r is an integer of 2-10.

20 In the formula (14), the alkyl group having 1 to 20 carbon atoms at \mathbf{R}^{16} is preferably exemplified by straight or branched chain alkyl having 2 to 19 carbon atoms, such as ethyl, propyl, t-butyl, t-amyl, t-nonyl, t-dodecyl, nonadecyl and the like and r is preferably 3 to 8.

25 Specific examples of dialkyl polysulfides of the formula (14) include diethyl pentasulfide, dipropyl tetrasulfide, di-tert-butyl disulfide, di-tert-butyl tetrasulfide, di-tert-amyl tetrasulfide, di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, di-tert-dodecyl pentasulfide, dinonadecyl tetrasulfide and the like.

30 In addition, polybutene having an average molecular weight of 200-1,000, paraffins, petrolatum, glycerin, polyhydric alcohols and fatty acid esters can be used as an elution regulator.

Examples of polybutene having an average molecular weight of 200-1,000 include LV-5, LV-10, LV-25, LV-50, LV-100,

HV-15, HV-35, HV-50, HV-100, HV-300 manufactured by NIPPON OIL COMPANY, LTD. and the like. Examples of paraffins include liquid paraffin, paraffin wax, paraffin chloride and the like. Examples of petrolatum include white petrolatum, yellow 5 petrolatum and the like.

Preferable examples of the above-mentioned elution regulator include di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, polybutene, liquid paraffin, white petrolatum and yellow petrolatum.

10 The above-mentioned elution regulator may be used alone or in combination of two or more thereof. The content of the above-mentioned elution regulator can be optionally changed according to the environment of application, which is preferably 1-30 wt%, more preferably 3-20 wt%, particularly 15 preferably 5-10 wt%, in a fishnet antifouling agent. When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 30 wt%, it unpreferably degrades property of a coating film.

B. Underwater antifouling coating

20 The underwater antifouling coating of the present invention shows low toxicity, is highly safe and shows a superior adhesion-preventive effect against coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, Serpula etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, 25 *Dexiospira spirillum* etc.); and other aquatic fouling organisms for a long time.

The underwater antifouling coating of the present invention can be prepared by adding a polymer containing 30 triphenylboron (1) or (2) in water-soluble resin or non-water-soluble resin, and mixing and dispersing them using a paint conditioner, homomixer and the like. In addition, an additive such as other component generally used for coating, solvent (xylene, methyl isobutyl ketone, n-butanol, butyl acetate etc.),

pigment (red iron oxide, titanium oxide, zinc oxide etc.), plasticizer, filler (talc, fine silica etc.), curing promoter and the like can be mixed as necessary.

The content of the polymer containing triphenylboron (1) or (2) in the underwater antifouling coating of the present invention can be optionally changed according to the environment of application, which is preferably 1 wt% - 80 wt%, more preferably 3 wt% - 40 wt%. When the content is less than 1 wt%, an adhesion-preventive effect against aquatic fouling organisms becomes insufficient, and conversely, when it exceeds 80 wt%, it increases the viscosity of the coating, which unpreferably makes handling difficult.

When the polymer containing triphenylboron (1) or (2) of the present invention is used as an underwater antifouling agent, a superior adhesion-preventive effect against aquatic fouling organisms can be achieved even by this polymer alone, but addition of silicone oil, elution regulator, an antifouling component other than a polymer containing triphenylboron (1) or (2) and the like allow exhibition of a more superior adhesion-preventive effect. Silicone oil, elution regulator, the antifouling components other than a polymer containing triphenylboron (1) or (2) and the like include those exemplified for fishnet antifouling agent. Where necessary, various resins explained with regard to the fishnet antifouling agent can be also added.

The content of the silicone oil can be optionally changed according to the environment of application, which is preferably 0.1 - 50 wt%, more preferably 0.5 - 25 wt%, in an underwater antifouling coating. When the content is less than 0.1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 50 wt%, it unpreferably degrades property of a coating film.

The weight ratio of the antifouling component other than the polymer containing triphenylboron (1) or (2) to the polymer

containing triphenylboron (1) or (2) of the present invention can be optionally changed according to the environment of application, which is preferably 1:50 - 50:1, more preferably 1:25 - 25:1, particularly preferably 1:10 - 10:1. When the 5 above-mentioned antifouling component is greater than the above-mentioned range, the property of a coating film is degraded, and conversely, when it is lower, an effect afforded by concurrent use is not expected undesirably.

The content of the elution regulator can be optionally 10 changed according to the environment of application, which is preferably 1 - 30 wt%, more preferably 3 - 20 wt%, particularly preferably 5-10 wt%, in an underwater antifouling coating. When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 15 30 wt%, it unpreferably degrades property of a coating film.

Examples

The present invention is explained in detail in the following by way of Examples and Comparative Examples. It is needless to say that the present invention is not limited by 20 these Examples. In the Examples, the contents are in wt%. In the Tables, triphenylboron is abbreviated as TPB.

Example 1 <synthesis of triphenylboron adduct>

Into a four neck 1 L flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was 25 placed an aqueous solution of sodium hydroxide adduct of triphenylboron (250.3 g, 9% aqueous solution, manufactured by Tokyo Kasei Co., Ltd.) and stirring was started. Ethylene diamine (4.81 g, manufactured by Tosoh Corporation) was dropwise added at room temperature from the dropping funnel. 30 After the dropwise addition, the mixture was stirred at the same temperature for 5 hr. The precipitate was collected by filtration and washed with water and dried to give white powdery substance (21.64 g). The obtained compound was subjected to elemental analysis and IR (infrared) spectrum

analysis. As a result, the compound was confirmed to be a triphenylboron-ethylenediamine adduct (triphenylboron adduct A) of the objective substance, m.p. 157.8-159.8°C.

Examples 2-4 <synthesis of triphenylboron adduct>

5 By synthesizing in the same manner as in Example 1 using the starting materials shown in Table 1, triphenylboron adducts B-D were obtained. They are shown in Table 1 together with triphenylboron adduct A. In Table 1, each figure is in g (gram).

10 Table 1 triphenylboron adduct

(unit:g)

		Example			
		1	2	3	4
amine	Ethylenediamine	4.81			
	Propylenediamine		5.93		
	P-phenylene-diamine			8.65	
	4-aminopyridine				7.53
TPB·NaOH adduct *1		250.3	250.3	250.3	250.3
Yield		21.64	21.38	24.21	24.28
Adduct reference		A	B	C	D

*1: sodium hydroxide adduct of triphenylboron, 9% aqueous solution

15 Example 5 <synthesis of polymer containing triphenylboron (1)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a solution (100 g) of methacrylic acid/methyl methacrylate/2-ethylhexyl acrylate copolymer (resin 1, M_w =ca 20,000, acid value 18.6 mg KOH/g) in 40% xylene/n-BuOH, and stirring was initiated. The triphenylboron-ethylenediamine adduct (triphenylboron adduct A, 10.1 g) synthesized in Example 1 was cast in at room temperature and then xylene (16.1 g) was added. The mixture was stirred at the same temperature for 5 25 hr to give a solution (polymer solution A, 126 g) of a polymer containing triphenylboron in xylene. The solvent was evaporated under reduced pressure from a part of the xylene

solution and the residue was dried to give a pale-yellow white resin like substance. By IR (infrared) spectrum analysis, it was confirmed to be the objective substance. The weight average molecular weight was about 13,000 (GPC). The IR (infrared) spectrum of this polymer is shown in Fig. 1.

Examples 6-15 <synthesis of polymers containing triphenylboron (1) and (2)>

In the same manner as in Example 5 using a triphenylboron adduct, a carboxyl group-containing polymer and a solvent shown 10 in Table 2, solutions of polymer containing a triphenylboron (polymer solutions B-K) were synthesized. They are collectively shown in Table 2 together with the polymer solution A. Unless particularly indicated, each figure in Table 2 is in g (gram).

15

Table 2 polymer containing triphenyboron
(unit: g unless specifically indicated)

	Example										
	5	6	7	8	9	10	11	12	13	14	15
TPB adduct	adduct A	10.1	12.6	10.5	16.1	10.5					
	adduct B					11.9	13.2				
	adduct C							11.6	14.6		
	adduct D									11.2	14.0
carboxyl group-containing polymer	Resin 1	100.0				100.0	100.0				
	Resin 2		20.0				20.0		20.0		20.0
	Resin 3		20.0								
	Resin 4		20.0								
solvent	Resin 5			50.0							
		16.1	48.9	45.8	54.2	90.8	18.9	49.7	18.4	51.9	17.8
yield (g)		126.0	81.2	76.0	90.0	151.0	130.3	82.4	130.0	86.2	129.0
	heating residue	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
weight average molecular weight (x10 ⁴)		1.3	1.6	1.8	8.2	1.4	1.4	1.7	1.5	1.7	1.4
basic constituting unit (%)		25.6	47.7	44.1	57.1	21.5	26.2	47.4	27.9	50.9	27.2
TPB content (%)		16.1	30.9	27.7	35.8	13.9	15.9	29.6	15.6	29.2	15.7
polymer solution reference	A	B	C	D	E	F	G	H	I	J	K

Resin 1: methacrylic acid/methyl methacrylate/2-ethylhexyl acrylate copolymer (solid content 40%, acid value 18.6 mg KOH/g)

Resin 2: ethylene/acrylic acid (15 wt%) copolymer

Resin 3: ethylene/methacrylic acid (15 wt%) copolymer

Resin 4: t-butyl acrylate/ethyl acrylate/methacrylic acid (23 wt%) copolymer

Resin 5: ethylene/acrylic acid (10 wt%, about 50% Zn salt) copolymer

solvent: xylene alone or xylene/nBuOH mixed system

Examples 16-29 and Comparative Examples 1-3 <FormulationExamples of fishnet antifouling agents>

The fishnet antifouling agents of the present invention (Examples 16-29) were prepared in the compositions shown in Table 3 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, fishnet antifouling agents of Comparative Examples 1-3 were prepared. Each figure in Table 3 is in wt%.

Table 3 fishnet antifouling agent

Compo- nent	Composition (wt%)										Comparative Example		
	Example										1	2	3
poly- mer	16	17	18	19	20	21	22	23	24	25	26	27	28
B	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6
solu- tion													
C													
D													
E													
F													
G													
H													
I													
J													
K													
TET													
PK													
TNPS	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
LV-50													
LR-155													
silicone	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
xylene	48.4	44.4	39.4	34.4	64.2	61.1	67.9	31.4	38.9	63.0	37.8	62.6	38.3

THIET: tetraethyl thiuram disulfide

PK: triphenylboron-pyridine adduct

TNPS: di-t-nonyl polysulfide (maximum value of occupancy)

LV-50: polybutene (Nippon Petrochemicals Co., Ltd.)

LR-155: acrylic resin (50% xylene solution, Mitsubishi Rayon Co., Ltd.)

silicone oil: polyether modified silicone oil

Examples 30-44 and Comparative Examples 4-7 <FormulationExamples of ship bottom antifouling coatings>

The ship bottom antifouling coating of the present invention (Examples 30-44) were prepared in the compositions shown in Table 4 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, ship bottom antifouling coatings of Comparative Examples 4-7 were prepared. Each figure in Table 4 is in wt%.

Table 4 ship bottom antifouling coating

	component	Coating composition (wt%)										Comparative Example							
		30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	4	5	6
polymer solution	A	50	50																
	B		50																
	C			50															
	D				50														
	E					50													
	F						50	50											
	G								50										
	H									50									
pigment	I										50								
	J											50							
	K												50						
	zinc oxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	red oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	colloidal silica	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	talc	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	known pollutant component	cuprous oxide	10																
resin	PK																		
	TPP-8																		
	viny1 resin varnish																		
	chlorinated isoprene rubber																		
	xylene	15	5	15	15	15	15	5	15	15	5	15	15	5	15	15	10	10	10
	MIBK	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	BuOH	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

PK: triphenylboron-pyridine adduct, MIBK: methyl isobutyl ketone
 TPP-8: triphenylboron-n-octylamine adduct, BuOH: n-butanol

Experimental Example 1 <fishnet antifouling agent effect test>

The fishnet antifouling agents of Examples 16-29 and Comparative Examples 1-3 were respectively applied to polyethylene unknotted nets (6 knot, 400 denier/60 yarns) by immersion, air-dried and set on a metal frame. The test nets were retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken and the degree of fouling due to adhesion of aquatic fouling organisms was observed. The degree of fouling was evaluated according to the following criteria, 10 the results of which are shown in Table 5.

Table 5 fishnet antifouling agent effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	16	A	A	A	A	B	B
	17	A	A	A	A	A	A
	18	A	A	A	A	A	A
	19	A	A	A	A	A	A
	20	A	A	A	A	A	A
	21	A	A	A	A	A	A
	22	A	A	A	A	A	A
	23	A	A	A	A	A	A
	24	A	A	A	A	A	A
	25	A	A	A	A	A	A
	26	A	A	A	A	A	A
	27	A	A	A	A	A	A
	28	A	A	A	A	A	A
	29	A	A	A	A	A	A
Comparative Example	1	C	D				
	2	A	A	B	C		D
	3	D					
untreated							

untreated: polyethylene unknotted net not treated with fishnet antifouling agent

15

Evaluation criteria of degree of fouling of net

Evaluation A: Area of fouling of fishnet, 0%, no adhesion of aquatic fouling organisms.

20

Evaluation B: Area of fouling of fishnet, over 0% to less than 10%, small amount of adhesion of aquatic fouling

organisms to the extent practically acceptable.

Evaluation C: Area of fouling of fishnet, 10% to less than 50%, great amount of adhesion of aquatic fouling organisms, unpractical as a fishnet.

5 Evaluation D: Area of fouling of fishnet, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms.

A number of aquatic fouling organisms such as barnacle and *Hydroides norvegica* adhered to the nets of Comparative 10 Examples 1-3 and untreated nets in 1 to 4 months. On the other hand, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the nets of Examples 16-29 retained underwater for at least 4 months.

Experimental Example 2 <ship bottom antifouling coating effect test>

The ship bottom antifouling coatings of Examples 30-44 and Comparative Examples 4-7 were applied on both sides of 50×100×2 mm hard vinyl chloride plates to achieve a dry film thickness of about 100 micron. After air-drying for one day, 20 these test plates were retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken and the degree of fouling of the test plates due to adhesion of aquatic organisms was observed. The degree of fouling was evaluated according to the following criteria, the results of which are 25 shown in Table 6.

Table 6 ship bottom antifouling coating effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	30	A	A	A	A	A	A
	31	A	A	A	A	A	A
	32	A	A	A	A	A	A
	33	A	A	A	A	A	A
	34	A	A	A	A	A	A
	35	A	A	A	A	A	A
	36	A	A	A	A	A	A
	37	A	A	A	A	A	A
	38	A	A	A	A	A	A
	39	A	A	A	A	A	A
	40	A	A	A	A	A	A
	41	A	A	A	A	A	A
	42	A	A	A	A	A	A
	43	A	A	A	A	A	A
	44	A	A	A	A	A	A
Comparative Example	4	A	A	A	B	B	C
	5	A	B	C	C	D	
	6	A	B	B	C	D	
	7	A	B	C	D		
untreated		D					

untreated: hard vinyl chloride plates not treated with ship
bottom antifouling coating

Evaluation criteria of degree of fouling of test plate

Evaluation A: Area of fouling of test plate, 0%, no adhesion
of aquatic fouling organisms.

Evaluation B: Area of fouling of test plate, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

Evaluation C: Area of fouling of test plate, 10% to less than 50%, great amount of adhesion of aquatic fouling organisms, impractical as a ship bottom antifouling coating.

Evaluation D: Area of fouling of test plate, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms.

A number of aquatic fouling organisms such as barnacle and *Hydroides norvegica* adhered to the plates of Comparative Examples 4-7 and untreated plates in 1 to 4 months. On the other hand, shellfish, tubicolous polychaetes or other aquatic 5 fouling organisms did not adhere at all to the plates of Examples 30-44 retained underwater for 6 months.

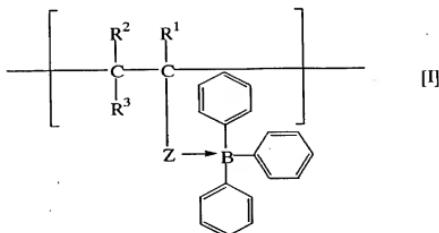
Industrial Applicability

As is evident from the foregoing explanation, the polymer containing triphenylboron (1) or (2) of the present 10 invention shows extremely small adhesion of coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, *Serpula* etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms 15 and shows a superior adhesion-preventive effect for a long time. Because it has a function of not only an active ingredient but also a binder, the polymer characteristically shows fine miscibility with other coating resins and a less adverse influence on the environment. Therefore, a fouling preventive 20 containing this polymer, such as a fishnet antifouling agent and an underwater antifouling coating (e.g., a ship bottom antifouling coating etc.), becomes extremely useful.

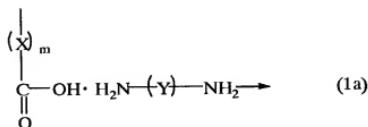
This application is based on patent application Nos. 25 1999-206799, 2000-76939 and 2000-80153 filed in Japan, the contents of which are hereby incorporated by reference.

WHAT IS CLAIMED IS

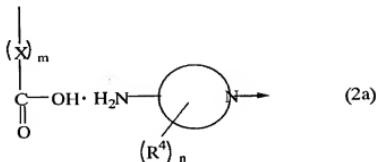
1. A polymer comprising a triphenylboron-containing constituting unit of the formula [I]:



5 wherein R¹, R² and R³ are the same or different and each is hydrogen atom or alkyl group having 1 to 4 carbon atoms;
 Z is a group of the formula (1a):



or the formula (2a):



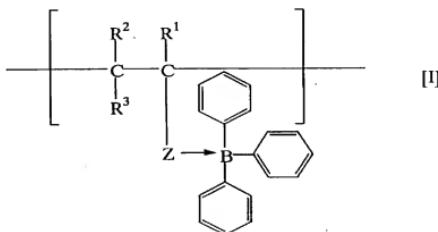
10 wherein, in the formulas (1a) and (2a), X is alkylene group having 1 to 18 carbon atoms, arylene group, aralkylene group, -C(=O)- group, -C(=O)-R⁵- group, -C(=O)-O-R⁵- group, -O-R⁵- group, -C(=O)-O-R⁵-O-C(=O)- group or -C(=O)-O-R⁵-O-C(=O)-R⁶- group (where R⁵ and R⁶ are the same or different and each is alkylene group having 1 to 18 carbon atoms or arylene group); Y

is alkylene group having 2 to 18 carbon atoms, arylene group, aralkylene group or cycloalkylene group; m is 0 or 1; R^4 in the number of n are the same or different and each is halogen atom or alkyl group having 1 to 18 carbon atoms; n is an integer of 5 0-3; and a group of the formula (2b):



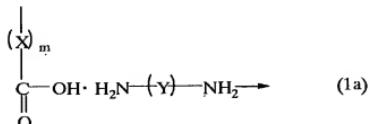
10 is amino-substituted, N-containing heterocycle.

2. The polymer of claim 1, which is expressed by the formula [I]:

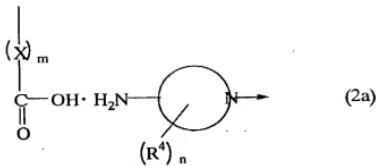


15 wherein R^1 , R^2 and R^3 are the same or different and each is hydrogen atom or methyl group;

Z is a group of the formula (1a):



or the formula (2a):



wherein, in the formulas (1a) and (2a), X is alkylene group having 1 to 18 carbon atoms, arylene group, aralkylene group, $-C(=O)-$ group, $-C(=O)-R^5-$ group, $-C(=O)-O-R^5-$ group, $-O-R^5-$ group, $-C(=O)-O-R^5-O-C(=O)-$ group or $-C(=O)-O-R^5-O-C(=O)-R^6-$ group (where R^5 and R^6 are the same or different and each is alkylene group having 1 to 18 carbon atoms or arylene group); Y is alkylene group having 2 to 18 carbon atoms, arylene group, aralkylene group or cycloalkylene group; m is 0 or 1; R^4 in the number of n are the same or different and each is halogen atom or alkyl group having 1 to 18 carbon atoms; n is an integer of 0-3; and a group of the formula (2b):



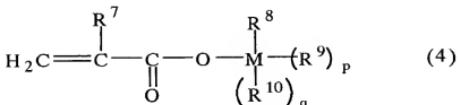
is amino-substituted, N-containing heterocycle.

3. The polymer of claim 1, wherein the weight average molecular weight is 1,000-1,000,000.

4. The polymer of claim 1, which further comprises a constituting unit derived from a polymerizable unsaturated monomer other than a constituting unit of the formula [I].

25

5. The polymer of claim 3, wherein the polymerizable unsaturated monomer has the formula (4):



wherein R^7 is hydrogen atom or alkyl group having 1 to 4 carbon atoms; M is metal atom or silicon atom; when M is metal atom, R^8 , R^9 and R^{10} are the same or different and each is organic acid residue, when M is silicon atom, R^8 , R^9 and R^{10} are the same or different and each is alkyl group having 1 to 18 carbon atoms, aryl group or cycloalkyl group; when M is divalent metal atom, p and q are both 0, when M is trivalent metal atom, p is 1 and q is 0, and when M is quaternary metal atom, both are 1.

10

6. The polymer of claim 5, wherein the metal atom is zinc, copper or magnesium.

15

7. A composition comprising the polymer of any of claims 1-6.

15

8. The composition of claim 7, further comprising at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

20

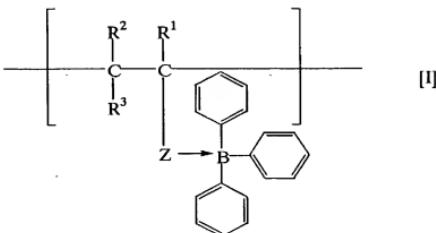
9. A fouling preventive comprising the polymer of any of claims 1-6.

25

10. The fouling preventive of claim 9, which further comprises at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

Abstract of the Disclosure

A polymer containing a triphenylboron-containing constituting unit of the formula [I]:



wherein each symbol is as defined in the specification, shows a superior adhesion-preventive effect against aquatic fouling organisms, such as coelenterates, shellfish, tubicolous polychaetes and the like, for a long time, shows a function of not only an active ingredient but also a binder, the polymer characteristically shows fine miscibility with other coating resins and a less adverse influence on the environment. Therefore, it can be used as a superior preventive of fouling due to the adhesion of aquatic fouling organisms.

SPECIFICATION

POLYMER CONTAINING TRIPHENYLBORON AND USE THEREOF

Technical Field

The present invention relates to a polymer containing triphenylboron and use thereof. More particularly, this invention relates to a preventive of fouling due to adhesion of aquatic fouling organisms (hereinafter to be also referred to as a fouling preventive), such as an antifouling agent for a fishnet, that prevents aquatic fouling organisms from adhering to and growing on culture and fixed fishnets, an underwater antifouling coating (e.g., ship bottom antifouling coating) that prevents aquatic fouling organisms from adhering to and growing on the bottom of a ship, a material used for a fishnet (e.g., buoy and rope), and condenser water channels of a nuclear energy or thermal power plant, and the like.

Background Art

When aquatic organisms such as coelenterates (e.g., hydrozoas, obelia etc.), shellfish, tubicolous polychaetes, algae, Polyzoa, Mollusca and the like adhere to the bottom of a ship, culture and fixed fishnets and the like, they cause a great economic loss to the ship and fishnets. Therefore, these aquatic organisms are called aquatic fouling organisms. For example, when barnacle and the like adhere to fishnets, the gaps are filled up. This may decrease oxygen in water by blocking the flow of tide, causing death of cultured fish from suffocation, or increase wave resistance, causing breakage and the like of the net when typhoon comes.

When these aquatic fouling organisms adhere to the ship bottom, the driving efficiency of the ship is decreased and fuel efficiency is decreased, which in turn results in economic loss. In an attempt to decrease the economic loss caused by the fouling organisms, therefore, great labor and cost have been expensed for the maintenance of objects susceptible to fouling, as the situation stands.

Various researches and suggestions have been heretofore made to prevent adhesion of aquatic fouling organisms. From the practical viewpoint, use of a series of organic tin compounds is effective. However, the organic tin compounds generally have strong toxicity to the extent that careless handling of products containing them can result in hazardous influence on the operator and that the environment may be contaminated.

These difficulties have produced the demand for a low-pollution preventive of fouling due to adhesion of aquatic fouling organisms, or an antifouling preventive, such as a low-pollution antifouling agent for a fishnet and a low-pollution underwater antifouling coating (e.g., ship bottom antifouling coating etc.). For example, JP-B-10849/1976 discloses an underwater antifouling coating containing a benzothiazole compound as an active ingredient; JP-A-38306/1985, JP-A-284275/1988 and JP-B-11606/1989 disclose various antifouling agents for fishnet and antifouling coating compositions, wherein a tetraalkyl thiuram disulfide compound and other compounds are combined; JP-B-50984/1986 discloses an anticontaminant agent for marine structures, which comprises a 3-isothiazolone compound as an active ingredient; and JP-B-20665/1989 and JP-B-24242/1990, and JP-A-9320/1978, JP-A-201804/1993, JP-A-100405/1994 and JP-A-100408/1994 disclose underwater antifouling coatings containing a maleimide compound as an active ingredient.

However, all of these antifouling agents only have a weak adhesion-preventive effect against coelenterates, such as hydrozoas, obelia and the like, and could not be used in a sea area where coelenterates live, such as the coasts of Tohoku region and Hokkaido. In Tokai and West Japan sea areas where lots of shellfish (e.g., barnacle, mussel etc.) and tubicolous polychaetes (e.g., *Hydroides norvegica* etc.) live, moreover, the conventional antifouling agents show weak adhesion

preventive effects and cannot effectively prevent adhesion of these aquatic fouling organisms.

It is conventionally known that cuprous oxide is effective against shellfish, and organic copper type 5 antifouling agents (e.g., copper pyrithion etc.) have been confirmed to be effective against shellfish and tubicolous polychaetes. However, cuprous oxide only shows a weak adhesion preventive effect against shellfish and tubicolous polychaetes. In addition, an organic copper group antifouling agent often 10 thickens or gelates a coating upon mixing with the coating, thereby posing a defect that mixing with a coating is difficult.

In addition, JP-A-8-295608 discloses a fishnet antifouling agent containing a triphenylboron alkylamine adduct compound as an active ingredient, JP-A-8-295609 discloses a 15 solution containing a triphenylboron octadecylamine adduct compound, and WO98/33892 discloses a triphenylboron-containing allylamine type polymer. However, sustained release of the active ingredient is difficult, and an antifouling effect cannot be maintained over a long time. Moreover, JP-A-11- 20 199801 discloses a triarylboron-containing polymer and JP-A-11-302571 discloses a resin bonded with a trisubstituted boron-containing-amine complex.

The present invention aims at solving the above-mentioned defects and providing an antifouling component exhibiting a 25 superior adhesion-preventive effect against aquatic fouling organisms such as coelenterates, shellfish, tubicolous polychaetes and the like and a fouling preventive containing this component, which is capable of retaining the effect for a long time.

30 The present invention also aims at providing an antifouling component superior in miscibility with other antifouling components, coating resins and the like, having a binder function and causing less adverse influence on the environment, and a fouling preventive containing this component.

Disclosure of the Invention

The present inventors have made intensive studies with the purpose of overcoming the above-mentioned various defects found in conventional fouling preventives, such as fishnet 5 antifouling agent, underwater antifouling coating and the like, and invented a novel polymer containing triphenylboron and a fouling preventive containing the same, that are associated with less possibility of environmental pollution, and show 10 superior adhesion-preventive effects against aquatic fouling organisms for a long time. That is, the present inventors have found that a novel triphenylboron-containing polymer shows a superior adhesion-preventive effect for a long time against coelenterates such as hydrozoas, obelia etc., shellfish such as barnacle, blue mussel, oyster, Serpula etc., tubicolous 15 polychaetes such as *Hydrodoides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc., and other aquatic fouling organisms, which resulted in the completion of the present invention. Particularly, a polymer having a triphenylboron-containing constituting unit of the formula (3) 20 below can afford a polymer having self-abrasive property and capable of exhibiting an antifouling effect for a long time, by copolymerization with a (meth)acrylic acid metal salt, rather than homopolymerization of triphenylboron-containing constituting units.

25 The polymer containing triphenylboron of the present invention has a triphenylboron-containing constituting unit, and has, in the same molecule, a resin moiety having a coating film-forming capability. Therefore, it can function not only as an active ingredient but also as a binder, and shows fine 30 miscibility with other coating resin and less adverse influence on the environment.

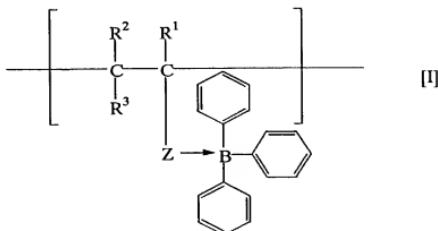
Brief Description of the Drawing

Fig. 1 shows an IR (infrared) spectrum of a polymer obtained in Example 5.

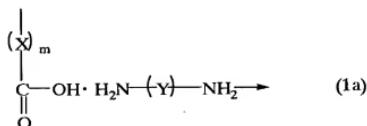
Fig. 2 shows an IR (infrared) spectrum of a polymer obtained in Example 45.

Embodiment of the Invention

The present invention relates to a polymer containing a 5 triphenylboron-containing constituting unit of the formula [I]:

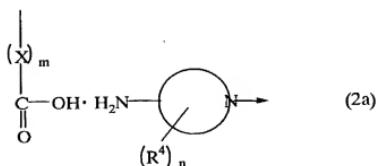


wherein R¹, R² and R³ are the same or different and each is hydrogen atom or alkyl group having 1 to 4 carbon atoms; Z is a group of the formula (1a):

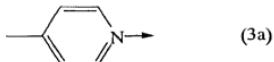


10

, the formula (2a):



or the formula (3a):



wherein, in the formulas (1a) and (2a), X is alkylene group having 1 to 18 carbon atoms, arylene group, aralkylene group, $-C(=O)-$ group, $-C(=O)-R^5-$ group, $-C(=O)-O-R^5-$ group, $-O-R^5-$ group, $-C(=O)-O-R^5-O-C(=O)-$ group or $-C(=O)-O-R^5-O-C(=O)-R^6-$ group (where R^5 and R^6 are the same or different and each is alkylene group having 1 to 18 carbon atoms or arylene group); Y is alkylene group having 2 to 18 carbon atoms, arylene group, aralkylene group or cycloalkylene group; m is 0 or 1; R^4 in the number of n are the same or different and each is halogen atom or alkyl group having 1 to 18 carbon atoms; n is an integer of 0-3; and a group of the formula (2b):



is amino-substituted, N-containing heterocycle, a composition containing the polymer and a fouling preventive containing the polymer.

20 The present invention is explained in detail in the following.

The alkyl group having 1 to 4 carbon atoms at R^1 , R^2 and R^3 in the formula [I] is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, 25 n-butyl, sec-butyl, tert-butyl and the like, with preference given to methyl.

Preferable examples of each of R^1 , R^2 and R^3 include hydrogen atom and methyl.

30 The halogen atom at R^4 in the formula (2a) is exemplified by chlorine atom, bromine atom, fluorine atom and the like. The alkyl group having 1 to 18 carbon atoms at R^4 is

exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-dodecyl, n-octadecyl and the like, with preference given to alkyl group having 1 to 4 carbon atoms. As R^4 , hydrogen atom or alkyl group having 1 to 4 carbon atoms is preferable. As n , 0 or 1 is preferable.

The alkylene group having 1 to 18 carbon atoms at X in the formulas (1a) and (2a) is exemplified by straight or 10 branched chain alkylene group such as methylene, ethylene, trimethylene, propylene, tetramethylene, 3-methyltetramethylene, octamethylene, dodecamethylene, octadecamethylene and the like, with preference given to alkylene group having 1 to 4 carbon atoms.

15 The arylene group at X in the formulas (1a) and (2a) is exemplified by o-phenylene, m-phenylene, p-phenylene, 1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference
20 given to p-phenylene.

The aralkylene group at X in the formulas (1a) and (2a) is exemplified by -Ar-Alk- or -Alk-Ar- where Ar is arylene group and Alk is alkylene group, such as benzylene ($-C_6H_4-CH_2-$ or $-CH_2-C_6H_4-$), phenethylene ($-C_6H_4-C_2H_5-$ or $-C_2H_5-C_6H_4-$) and the like, with preference given to benzylene.

The alkylene group having 1 to 18 carbon atoms at R^5 and R^6 of $-C(=O)-R^5-$ group, $-C(=O)-O-R^5-$ group, $-O-R^5-$ group, $-C(=O)-O-R^5-O-C(=O)-$ group or $-C(=O)-O-R^5-O-C(=O)-R^6-$ group for X in the formulas (1a) and (2a) is exemplified by straight or 30 branched chain alkylene group such as methylene, ethylene, trimethylene, propylene, tetramethylene, 2-methyltetramethylene, 3-methyltetramethylene, octamethylene, dodecamethylene, octadecamethylene and the like, with preference given to alkylene group having 1 to 4 carbon atoms.

The arylene group at R⁵ and R⁶ of -C(=O)-R⁵- group, -C(=O)-O-R⁵- group, -O-R⁵- group, -C(=O)-O-R⁵-O-C(=O)- group or -C(=O)-O-R⁵-O-C(=O)-R⁶- group for X in the formulas (1a) and (2a) is exemplified by o-phenylene, m-phenylene, p-phenylene, 5 1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference given to p-phenylene.

The X in the formulas (1a) and (2a) may be void (m=0) or 10 preferable alkylene group having 1 to 4 carbon atoms.

The alkylene group having 2 to 18 carbon atoms at Y in the formula (1a) is exemplified by alkylene such as ethylene, trimethylene, propylene, tetramethylene, pentamethylene, hexamethylene, octamethylene, dodecamethylene, 15 octadecamethylene and the like, with preference given to ethylene and propylene.

The arylene group at Y in the formula (1a) is exemplified by o-phenylene, m-phenylene, p-phenylene, 1,8-naphthylene, 1,7-naphthylene, 1,6-naphthylene, 1,4-naphthylene, 1,3-naphthylene, 20 1,2-naphthylene, 2,3-naphthylene, 2,6-naphthylene, 2,7-naphthylene and the like, with preference given to p-phenylene.

The aralkylene group at Y in the formula (1a) is exemplified by -Ar-Alk- or -Alk-Ar- where Ar is arylene group and Alk is alkylene group, such as benzylene (-C₆H₄-CH₂- or 25 -CH₂-C₆H₄-), phenethylene (-C₆H₄-C₂H₅- or -C₂H₅-C₆H₄-) and the like, with preference given to benzylene.

The cycloalkylene group at Y in the formula (1a) preferably has 3-10 carbon atoms, such as cyclopropylene, cyclobutylene, cyclohexylene, cyclooctylene, cyclodecylene and 30 the like, with preference given to cyclohexylene.

The Y in the formula (1a) is preferably ethylene, propylene or p-phenylene.

The N-containing heterocycle of the amino-substituted, N-containing heterocycle in the formula (2b) may be a

monoheterocycle or condensed heterocycle, or saturated heterocycle or unsaturated heterocycle, or may contain sulfur atom or oxygen atom. Preferably, it is a 5 or 6-membered ring or a condensed ring containing the same, such as pyridine ring, 5 pyrimidine ring, pyrrole ring, pyrazole ring, pyrrolidine ring, pyrazoline ring, piperidine ring, piperazine ring, pyrazine ring, purine ring, imidazole ring, benzimidazole ring, indole ring, indazole ring, triazole ring, carbazole ring, phenothiazine ring, phenoxazine ring, quinoline ring and the 10 like, with preference given to pyridine ring and piperidine ring.

The alkyl group having 1 to 4 carbon atoms at R^7 in the formula (4) is exemplified by straight or branched chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-15 butyl, tert-butyl and the like, with preference given to methyl. As R^7 , hydrogen atom and methyl are preferable.

The organic acid residue at R^8 , R^9 and R^{10} in the formula (4) refers to the residue of carboxyl of organic acid after eliminating hydrogen atom, wherein the organic acid is 20 exemplified by optinally substituted saturated and unsaturated aliphatic carboxylic acid having 1 to 18 carbon atoms such as acrylic acid, methacrylic acid, propionic acid, octyl acid, versatic acid, stearic acid, isostearic acid, palmitic acid, monochloroacetic acid, monofluoroacetic acid and the like; 25 optionally substituted aromatic carboxylic acid such as benzoic acid, α -naphthoic acid, β -naphthoic acid, nitrobenzoic acid, nitronaphthalenecarboxylic acid, salicylic acid, cresotinic acid and the like; optionally substituted aromatic aliphatic carboxylic acid such as 2,4-dichlorophenoxyacetic acid, 2,4,5-30 trichlorophenoxyacetic acid and the like; heterocyclecarboxylic acid such as quinolinecarboxylic acid and the like; pyruvic acid and the like.

The alkyl group having 1 to 18 carbon atoms at R^8 , R^9 and R^{10} in the formula (4) is exemplified by straight or branched

chain alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, hexyl, octyl, 2-ethylhexyl, dodecyl, octadecyl and the like.

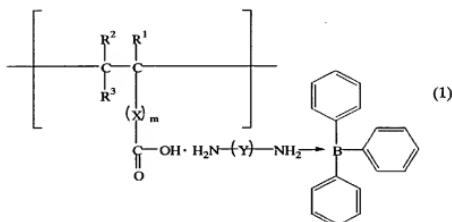
The aryl group at R^8 , R^9 and R^{10} in the formula (4) is exemplified by phenyl, naphthyl and the like.

The cycloalkyl group at R^8 , R^9 and R^{10} in the formula (4) is exemplified by those having 3 to 10 carbon atoms, such as cyclopropyl, cyclohexyl, cyclooctyl, cyclododecyl and the like.

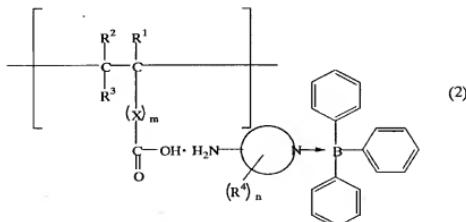
The metal atom at M in the formula (4) is exemplified by Cu, Zn, Fe, Ni, Co, Pb, Al, Mg and the like, with preference given to Cu, Zn and Mg.

When M is a metal atom, R^8 , R^9 and R^{10} are preferably aliphatic carboxylic acid residue having 1 to 18 carbon atoms, and when M is a silicon atom, R^8 , R^9 and R^{10} are preferably alkyl group having 1 to 4 carbon atoms.

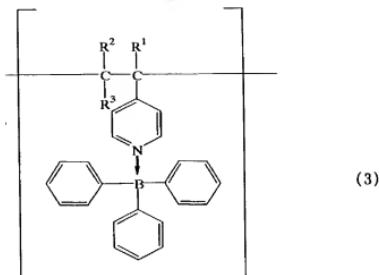
As the polymer containing triphenylboron of the present invention, there is mentioned a polymer containing a triphenylboron-containing constituting unit of the following the formula (1):



20 , the formula (2):



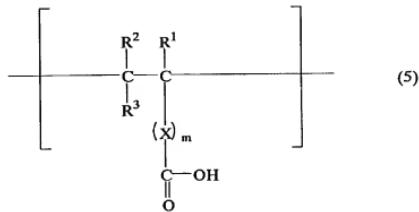
or the formula (3):



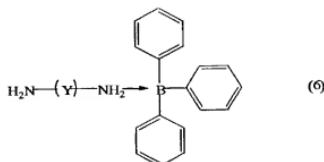
wherein each symbol in the formulas (1)–(3) is as defined above.

Polymer containing triphenylboron (1)

In the polymer containing a triphenylboron-containing 5 constituting unit of the formula (1) (hereinafter to be also referred to as a polymer containing triphenylboron (1)) of the present invention, triphenylboron-containing constituting unit of the formula (1) consists of a carboxyl group-containing constituting unit of the formula (5):



10 wherein each symbol is as defined above, and a diamine adduct of triphenylboron of the formula (6):



wherein each symbol is as defined above.

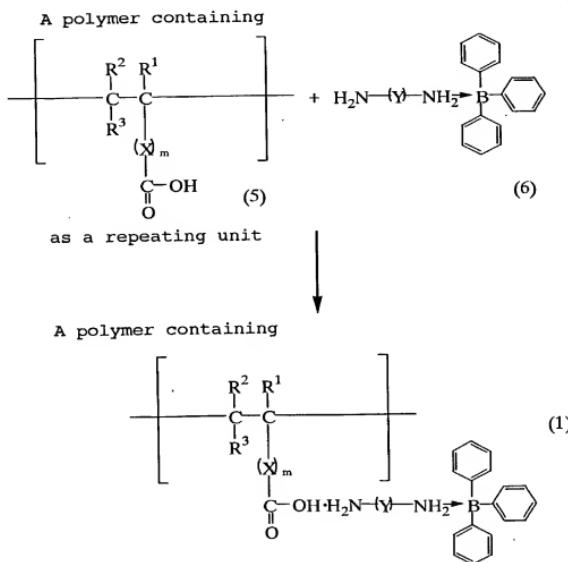
The carboxyl group-containing constituting unit of the formula (5) is exemplified by constituting units derived from carboxyl group-containing polymerizable unsaturated monomer, such as acrylic acid, crotonic acid, isocrotonic acid, 5 vinylacetic acid, methacrylic acid, 2-ethylacrylic acid, 2-n-propylacrylic acid, 2-isopropylacrylic acid, 2-n-butylacrylic acid, 2-sec-butylacrylic acid, 2-tert-butylacrylic acid, 2-ethyl-2-butenoic acid, 2-n-propyl-2-butenoic acid, 2-isopropyl-2-butenoic acid, 2-n-butyl-2-butenoic acid, 2-sec-butyl-2-butenoic acid, 2-tert-butyl-2-butenoic acid, 2-pentenoic acid, 2-methyl-2-pentenoic acid, 3-methyl-2-pentenoic acid, 4-methyl-2-pentenoic acid, 2-ethyl-2-pentenoic acid, 2-n-propyl-2-pentenoic acid, 2-isopropyl-2-pentenoic acid, 2-n-butyl-2-pentenoic acid, 2-sec-butyl-2-pentenoic acid, 2-tert-butyl-2-pentenoic acid, 3-pentenoic acid, 4-methyl-3-pentenoic acid, 2-hexenoic acid, 2-methyl-2-hexenoic acid, 2-ethyl-2-hexenoic acid, 2-n-propyl-2-hexenoic acid, 2-isopropyl-2-hexenoic acid, 2-n-butyl-2-hexenoic acid, 2-sec-butyl-2-hexenoic acid, 2-tert-butyl-2-hexenoic acid, 3-hexenoic acid, 4-hexenoic acid, 5-hexenoic acid, 2-heptenoic acid, 2-methyl-2-heptenoic acid, 2-ethyl-2-heptenoic acid, 2-n-propyl-2-heptenoic acid, 2-isopropyl-2-heptenoic acid, 2-n-butyl-2-heptenoic acid, 2-sec-butyl-2-heptenoic acid, 2-tert-butyl-2-heptenoic acid, 3-heptenoic acid, 4-heptenoic acid, 5-heptenoic acid, 6-heptenoic acid, 4-methyl-2-hexenoic acid, 5-methyl-2-hexenoic acid, 4,4-dimethyl-2-pentenoic acid, 2,4-dimethyl-2-pentenoic acid, 2,4-dimethyl-2-hexenoic acid, 2,5-dimethyl-2-hexenoic acid, 2,4,4-trimethyl-2-pentenoic acid, 3-methyl-2-butenoic acid, 2,3-dimethyl-2-butenoic acid, 3-methyl-2-pentenoic acid, 2,3-dimethyl-2-pentenoic acid, 3-methyl-2-hexenoic acid, 2,3-dimethyl-2-hexenoic acid, 3,4-dimethyl-2-pentenoic acid, 2,3,4-trimethyl-2-pentenoic acid, 3-methyl-2-heptenoic acid, 2,3-dimethyl-2-heptenoic acid, 3,4-dimethyl-2-hexenoic acid, 2,3,4-trimethyl-2-hexenoic acid, 3,5-dimethyl-2-hexenoic acid, 2,3,5-

trimethyl-2-hexenoic acid, 3,4,4-trimethyl-2-pentenoic acid,
 2,3,4,4-tetramethyl-2-pentenoic acid, 7-octenoic acid, 11-
 dodecenoic acid, 15-hexadecenoic acid, 17-octadecenoic acid, 2-
 methyl-3-butenoic acid, 2-methyl-4-pentenoic acid, 2-methyl-5-
 5 hexenoic acid, 2-methyl-6-heptenoic acid, 2-methyl-7-octenoic
 acid, 2-methyl-11-dodecenoic acid, 2-methyl-15-hexadecenoic
 acid, 2-methyl-17-octadecenoic acid, 4-vinylbenzoic acid, 4-(1-
 propenyl)benzoic acid, 4-(isopropenyl)benzoic acid, 4-(1-
 methyl-1-propenyl)benzoic acid, 4-(2-methyl-1-propenyl)benzoic
 10 acid, 4-vinylphenylacetic acid, 4-(1-propenyl)phenylacetic acid,
 4-(isopropenyl)phenylacetic acid, 4-(1-methyl-1-
 propenyl)phenylacetic acid, 4-(2-methyl-1-propenyl)phenylacetic
 acid, 2-oxo-3-butenoic acid, 3-oxo-4-pentenoic acid, 4-oxo-5-
 hexenoic acid, carboxymethyl acrylate, 2-carboxyethyl acrylate,
 15 3-carboxypropyl acrylate, 4-carboxybutyl acrylate, 5-
 carboxypentyl acrylate, 6-carboxyhexyl acrylate, 7-
 carboxyheptyl acrylate, 8-carboxyoctyl acrylate, 12-
 carboxydodecyl acrylate, 18-carboxyoctadecyl acrylate, o-
 carboxyphenyl acrylate, m-carboxyphenyl acrylate, p-
 20 carboxyphenyl acrylate, 2-vinyloxyacetic acid, 3-
 vinyloxypropionic acid, monoacryloyloxyethyl oxalate, mono-3-
 acryloyloxypropyl oxalate, monoacryloyloxyethyl malonate,
 mono-3-acryloyloxypropyl malonate and the like, with preference
 given to constituting unit derived from acrylic acid and
 25 methacrylic acid. These constituting units may be contained
 solely or in combination of two or more kinds thereof in a
 polymer.

The diamine of the formula (7) below of the diamine
 adduct of triphenylboron expressed by the formula (6) is
 30 exemplified by alkylenediamines having 2 to 18 carbon atoms,
 such as ethylenediamine, propylenediamine, trimethylenediamine,
 tetramethylenediamine, 1,3-diaminobutane, 2,3-diaminobutane,
 pentamethylenediamine, 2,4-diaminopentane, hexamethylenediamine,
 octamethylenediamine, dodecamethylenediamine,

octadecamethylenediamine and the like; arylenediamines such as phenylenediamines (e.g., m-phenylenediamine, p-phenylenediamine etc.), naphthylenediamines (e.g., 1,4-diaminonaphthalene, 1,5-diaminonaphthalene etc.), and the like; aminoaralkylamines such as aminobenzylamines (e.g., 3-aminobenzylamine, 4-aminobenzylamine etc.), aminophenethylamines (e.g., 3-aminophenethylamine, 4-aminophenethylamine etc.), and the like; diaminocycloalkanes such as 1,3-diaminocyclohexane, 1,4-diaminocyclohexane and the like; and the like, with preference given to ethylenediamine, propylenediamine and p-phenylenediamine.

The polymer containing triphenylboron (1) of the present invention can be synthesized by, for example, the following method.



as a repeating unit

wherein each symbol is as defined above.

That is, the polymer containing triphenylboron (1) can be obtained by adding dropwise a diamine adduct of triphenylboron of the formula (6) or a solution thereof to a 5 solution of polymer containing a carboxyl group-containing constituting unit of the formula (5) (hereinafter this polymer is sometimes to be referred to as a carboxyl group-containing polymer) to allow reaction and removing the solvent by distilling away under reduced pressure.

10 In the above-mentioned method, the diamine adduct of triphenylboron of the formula (6) is preferably used in an amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to the carboxyl group of the polymer containing the carboxyl group-containing constituting unit of the formula 15 (5). When this amount of use is less than 0.1 equivalent, adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, when it exceeds 3.0 equivalents, unreacted diamine adduct of triphenylboron remains excessively and the prevention 20 of adhesion is no longer efficient even if increase in addition efficiency is taken into consideration.

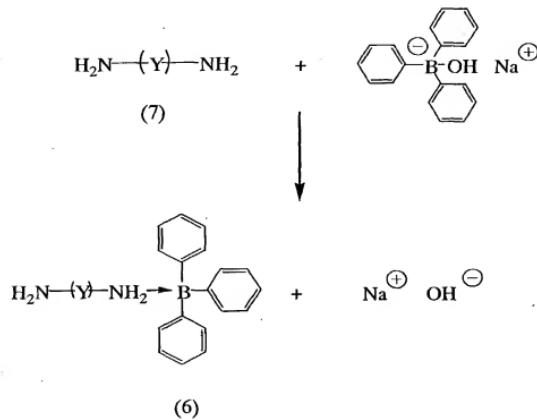
The solvent to be used in the above-mentioned method is not particularly limited as long as it does not affect the reaction adversely. For example, xylene, n-butanol, toluene, 25 chloroform, propylene glycol monomethyl ether and the like are mentioned, which may be used alone or in combination of two or more kinds thereof.

The temperature of reaction between diamine adduct of triphenylboron of the formula (6) and a polymer containing a 30 carboxyl group-containing constituting unit of the formula (5) is generally room temperature, and can be changed to 100°C as necessary. The reaction time is generally from about 30 minutes to 24 hours.

The polymer containing a carboxyl group-containing

constituting unit of the formula (5) is obtained by polymerizing a polymerizable unsaturated monomer including the above-mentioned carboxyl group-containing polymerizable unsaturated monomer by a conventionally-known method.

5 The diamine adduct of triphenylboron of the formula (6) can be synthesized by, for example, the method shown by the following formulas.



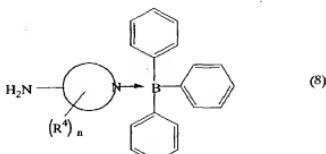
wherein each symbol is as defined above

That is, the diamine adduct of triphenylboron of the formula (6) can be obtained by adding dropwise diamine of the formula (7) to an aqueous solution of a sodium hydroxide adduct of triphenylboron, and when the objective substance precipitated as an insoluble material, by collecting the insoluble material by filtration, washing with water and 15 drying, and when the objective substance is dissolved, by partitioning and removing the solvent by distilling away under reduced pressure.

Polymer containing triphenylboron (2)

The triphenylboron-containing constituting unit of the formula (2) of the polymer containing a triphenylboron-containing constituting unit of the formula (2) (hereinafter to

be also referred to as a polymer containing triphenylboron (2)) of the present invention consists of the carboxyl group-containing constituting unit of the above-mentioned formula (5), and an N-containing heterocyclic adduct of triphenylboron of the formula (8):

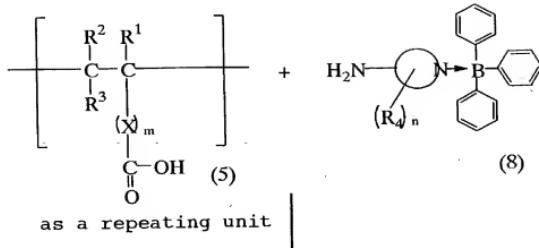


wherein each symbol is as defined above, which is an adduct of triphenylboron and an amino group-substituted, N-containing heterocycle of the formula (9) to be mentioned below.

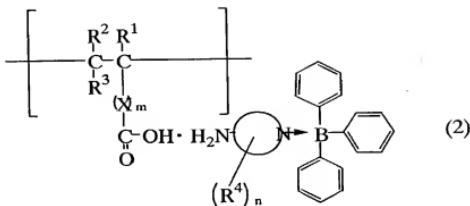
10 The amino group-substituted, N-containing heterocycle of
the N-containing heterocyclic adduct of triphenylboron of the
formula (8) is, for example, 3-aminopyridine, 4-aminopyridine,
4-aminopyrimidine, 5-aminopyrimidine, 3-aminopyrazole, 4-
aminopyrazole, 4-aminoimidazole, 4-aminoindazole, 5-
15 16 aminoindazole, 4-aminoindole, 5-aminoindole, 4-
aminobenzimidazole, 3-aminopyrrolidine, 3-aminopiperidine, 4-
aminopiperidine, 3-aminouquinoline, 5-aminouquinoline, 1-
aminopiperazine, aminopyrazine, 2-aminopurine, 3-aminopyrrole,
3-aminopyrazoline, 3-amino-1,2,4-triazole, 4-amino-1,2,4-
20 triazole, 4-aminocarbazole, 4-aminophenothiazine, 4-
aminophenoxazine and the like, with preference given to 4-
aminopyridine and 4-aminopiperidine.

The polymer containing triphenylboron (2) of the present invention can be synthesized by, for example, the following 25 method.

A polymer containing



a polymer containing



as a repeating unit

wherein each symbol is as defined above.

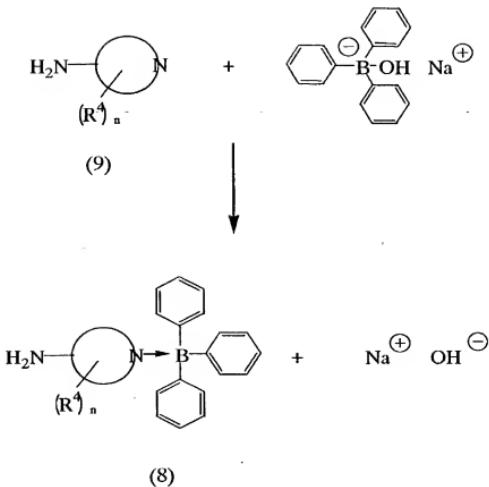
That is, the polymer containing triphenylboron (2) can be obtained by adding dropwise an N-containing heterocyclic adduct of triphenylboron of the formula (8) or a solution thereof to a solution of polymer containing a carboxyl group-containing constituting unit of the formula (5) to allow reaction and removing the solvent by distilling away under reduced pressure.

In the above-mentioned method, the N-containing heterocyclic adduct of triphenylboron of the formula (8) is preferably used in an amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to the carboxyl group of the 5 polymer containing the carboxyl group-containing constituting unit of the formula (5). When this amount of use is less than 0.1 equivalent, adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, when it exceeds 3.0 equivalents, 10 unreacted N-containing heterocyclic adduct of triphenylboron remains excessively and the prevention of adhesion is no longer efficient even if increase in addition efficiency is taken into consideration.

The solvent to be used in the above-mentioned method is 15 not particularly limited as long as it does not affect the reaction adversely. For example, xylene, toluene, chloroform, n-butanol, propylene glycol monomethyl ether and the like are mentioned, which may be used alone or in combination of two or more kinds thereof.

20 The temperature of reaction between N-containing heterocyclic adduct of triphenylboron of the formula (8) and a polymer having a carboxyl group-containing constituting unit of the formula (5) is generally room temperature, and can be changed to 100°C as necessary. The reaction time is generally 25 from about 30 minutes to 24 hours.

The N-containing heterocyclic adduct of triphenylboron of the formula (8) can be synthesized by, for example, the following method:



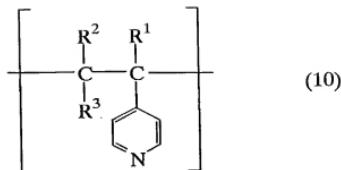
wherein each symbol is as defined above.

That is, N-containing heterocyclic adduct of

5 triphenylboron of the formula (8) is obtained by adding the
amino-substituted, N-containing heterocycle of the formula (9)
to an aqueous solution of a sodium hydroxide adduct of
triphenylboron, and washing with water and drying the
precipitated insoluble material.

10 Polymer containing triphenylboron (3)

The triphenylboron-containing constituting unit of the formula (3) in the polymer containing a triphenylboron-containing constituting unit of the formula (3) of the present invention (hereinafter to be also referred to as a polymer 15 containing triphenylboron (3)) consists of a constituting unit derived from a vinylpyridine derivative of the formula (10):

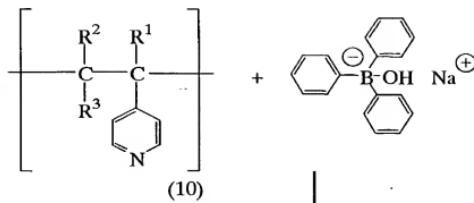


wherein each symbol is as defined above, and triphenylboron.

The vinylpyridine derivative of the constituting unit derived from vinylpyridine derivative of the formula (10) is exemplified by 4-vinylpyridine, 4-(1-methylvinyl)pyridine, 4-(2-methylvinyl)pyridine, 4-(1,2-dimethylvinyl)pyridine, 4-(1-ethylvinyl)pyridine, 4-(2-ethylvinyl)pyridine, 4-(1-butylvinyl)pyridine and the like.

The polymer containing triphenylboron of the present invention (3) can be synthesized by, for example, the following method.

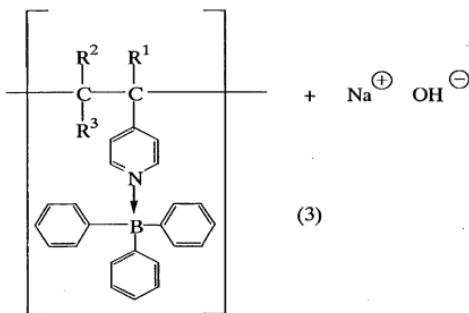
A polymer containing



as a repeating unit



a polymer containing



as a repeating unit

wherein each symbol is as defined above.

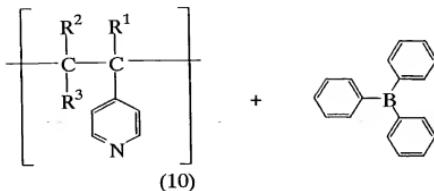
That is, the polymer containing triphenylboron (3) can be obtained by adding dropwise an aqueous solution of sodium hydroxide adduct of triphenylboron of the formula (3) to a solution of polymer containing a constituting unit derived from vinylpyridine derivative of the formula (10), and when the objective substance precipitated as an insoluble material, by collecting the insoluble material by filtration, washing with water and drying, and when the objective substance is dissolved, by partitioning and removing the solvent by

distilling away under reduced pressure.

In the above-mentioned method, the sodium hydroxide adduct of triphenylboron is preferably used in an amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to 5 the pyridyl group of the polymer containing constituting unit derived from vinylpyridine derivative of the formula (10). When this amount of use is less than 0.1 equivalent, adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, 10 when it exceeds 3.0 equivalents, unreacted sodium hydroxide adduct of triphenylboron remains excessively and the prevention of adhesion is no longer efficient even if increase in addition efficiency is taken into consideration.

In addition, the polymer containing triphenylboron (3) of 15 the present invention can also be synthesized by the following method.

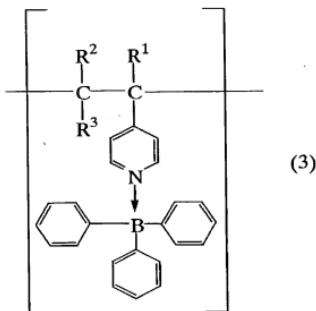
A polymer containing



as a repeating unit



a polymer containing



as a repeating unit

wherein each symbol is as defined above.

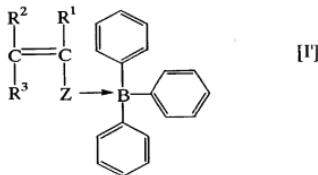
That is, the polymer containing triphenylboron (3) can be synthesized by reacting a polymer containing a constituting unit derived from a vinylpyridine derivative of the formula (10) and triphenylboron in an organic solvent such as toluene, xylene, chloroform, dimethylsulfoxide, n-butanol, propylene glycol monomethyl ether and the like.

In the above-mentioned method, triphenylboron is preferably used in an amount of 0.1-3.0 equivalents, more preferably 0.5-2.0 equivalents, to the pyridyl group of the polymer containing a constituting unit derived from a vinylpyridine derivative of the formula (10). When this amount of use is less than 0.1 equivalent, adhesion of aquatic fouling organisms may not be prevented effectively due to the insufficient content of triphenylboron. Conversely, when it exceeds 3.0 equivalents, unreacted triphenylboron remains excessively and the prevention of adhesion is no longer efficient even if increase in addition efficiency is taken into consideration.

The temperature of reaction between a polymer containing a constituting unit derived from a vinylpyridine derivative of the formula (10) and triphenylboron or a sodium hydroxide adduct thereof is generally room temperature, and can be changed to 100°C as necessary. The reaction time is generally from about 30 minutes to 24 hours.

The above-mentioned polymers containing triphenylboron (1)-(3) can be produced by the following method, besides the above-mentioned production method. That is, the above-mentioned polymers containing triphenylboron (1)-(3) can be synthesized by homopolymerization of a triphenylboron-containing vinyl monomer of the formula [I']:

25

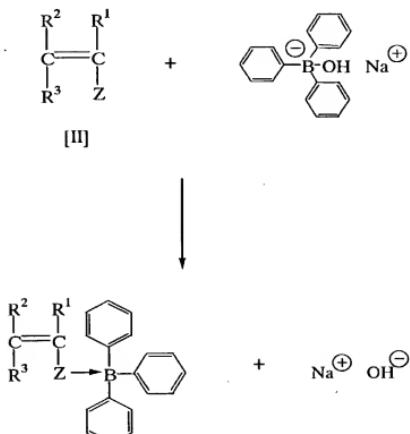


wherein each symbol is as defined above, or copolymerization of this monomer and a different polymerizable unsaturated monomer.

The above-mentioned triphenylboron-containing vinyl

monomer of the formula [I'] can be synthesized by the following three methods.

Method 1:



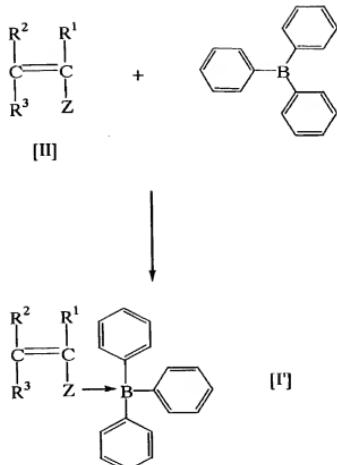
[II]

[I']

wherein each symbol is as defined above.

5 The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by adding dropwise a solution containing vinyl compound of the above-mentioned formula [II] to an aqueous solution of sodium hydroxide adduct of triphenylboron, and when the objective substance precipitated 10 as an insoluble material, by collecting the insoluble material by filtration, washing with water and drying, and when the objective substance is dissolved, by partitioning and removing the solvent by distilling away under reduced pressure.

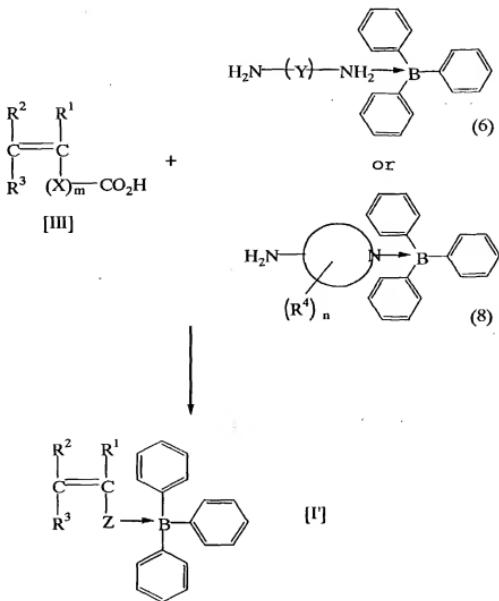
Method 2:



wherein each symbol is as defined above.

The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by reacting the vinyl compound of the above-mentioned formula [II] and triphenylboron in an organic solvent such as toluene, xylene, chloroform, dimethylsulfoxide, n-butanol, propylene glycol monomethyl ether and the like.

Method 3 (when substituent Z is a group of the formula (1a) or (1b)):



wherein each symbol is as defined above.

5 The triphenylboron-containing vinyl monomer of the formula [I'] can be obtained by reacting the vinyl compound of the above-mentioned formula [III] and a diamine adduct of triphenylboron of the formula (6) or N-containing heterocyclic adduct of triphenylboron of the formula (8).

10 The triphenylboron to be used in the present invention may be commercially available or can be produced by reacting boron trifluoride and phenylmagnesium bromide.

The polymers containing triphenylboron (1)-(3) of the present invention have a weight average molecular weight of

preferably 1,000-1,000,000, particularly preferably 3,000-500,000. When the molecular weight is less than 1,000, the coating film formed becomes brittle, and conversely, when it exceeds 1,000,000, the polymer solution has a higher viscosity, which unpreferably makes its handling difficult.

The content of the triphenylboron-containing constituting unit of the formula (1), (2) or (3) in the polymer containing triphenylboron (1)-(3) of the present invention is each preferably not less than 1.0 wt%, more preferably 5-95 wt%, particularly preferably 5-70 wt%. When the content is less than 1.0 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient.

The content of the triphenylboron in the polymer containing triphenylboron (1) and (2) of the present invention is each preferably not less than 0.5 wt%, more preferably 3-60 wt%, particularly preferably 3-45 wt%. When the content is less than 0.5 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient.

The content of the triphenylboron in the polymer containing triphenylboron (3) of the present invention is preferably 0.02-70 wt%, more preferably 0.5-70 wt%, most preferably 3-65 wt%, particularly preferably 3-50 wt%. When the content is less than 0.02 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient. It is impossible for the content to exceed 70 wt%.

The polymers containing triphenylboron (1)-(3) of the present invention may contain a constituting unit derived from a polymerizable unsaturated monomer other than the triphenylboron-containing constituting unit of the formula (1), (2) or (3). By containing such constituting unit, the triphenylboron content of the polymers containing triphenylboron (1)-(3) can be adjusted. Therefore, a polymer containing a carboxyl group-containing constituting unit of the

formula (5) and a polymer containing a constituting unit derived from a vinylpyridine derivative of the formula (10) may be a homopolymer or a copolymer. The copolymer is obtained by copolymerizing the aforementioned carboxyl group-containing

5 polymerizable unsaturated monomer and a polymerizable unsaturated monomer other than the carboxyl group-containing polymerizable unsaturated monomer or by copolymerizing a vinylpyridine derivative and a polymerizable unsaturated monomer other than the vinylpyridine derivative.

10 The constituting unit derived from a polymerizable unsaturated monomer other than the triphenylboron-containing constituting unit of the formula (1), (2) or (3) is, for example, a constituting unit derived from a polymerizable unsaturated monomer without boron. Such polymerizable

15 unsaturated monomer is, for example, vinyl hydrocarbons such as ethylene, propylene, butadiene, isoprene, styrene, α -methylstyrene, vinyltoluene, divinylbenzene, indene and the like; acrylonitriles such as acrylonitrile, methacrylonitrile and the like; unsaturated carboxylic acids such as acrylic acid, 20 crotonic acid, isocrotonic acid, methacrylic acid, vinylacetic acid, vinylpropionic acid, vinylbutyric acid, p-vinylbenzoic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid and the like; unsaturated carboxylic anhydrides such as maleic anhydride, itaconic anhydride, citraconic 25 anhydride and the like; vinyl heterocyclic compounds such as 2-vinylpyridine, 4-vinylpyridine, N-vinyl-2-pyrrolidone, vinylcarbazole and the like; vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl benzoate and the like;

30 halogenated vinyls such as vinyl chloride, vinylidene chloride and the like; vinylamines; allylamines; vinyl alcohols; allyl alcohols; vinyl ketones such as methyl vinyl ketone, phenyl vinyl ketone and the like; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, lauryl vinyl

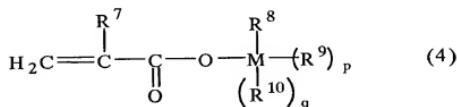
ether, phenyl vinyl ether, benzyl vinyl ether and the like; acrylic acid esters such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, cetyl acrylate, stearyl acrylate, vinyl acrylate, benzyl acrylate, phenyl acrylate, isobornyl acrylate, cyclohexyl acrylate, glycidyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxybutyl acrylate, 4-hydroxybutyl acrylate, glycerol acrylate, butylaminoethyl acrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminopropyl acrylate, dimethylaminobutyl acrylate, dibutylaminoethyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, phenoxyethyl acrylate, 2-(2-ethylhexyloxy)ethyl acrylate, 1-methyl-2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 3-methyl-3-methoxybutyl acrylate, o-methoxyphenyl acrylate, m-methoxyphenyl acrylate, p-methoxyphenyl acrylate, o-methoxyphenylethyl acrylate, m-methoxyphenylethyl acrylate, p-methoxyphenylethyl acrylate and the like; methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, vinyl methacrylate, benzyl methacrylate, phenyl methacrylate, isobornyl methacrylate, cyclohexyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxybutyl methacrylate, 4-hydroxybutyl methacrylate, glycerol methacrylate, butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, dimethylaminobutyl methacrylate, dibutylaminoethyl methacrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, phenoxyethyl methacrylate, 2-(2-ethylhexyloxy)ethyl methacrylate, 1-methyl-2-methoxyethyl

methacrylate, 3-methoxybutyl methacrylate, 3-methyl-3-methoxybutyl methacrylate, o-methoxyphenyl methacrylate, m-methoxyphenyl methacrylate, p-methoxyphenyl methacrylate, o-methoxyphenylethyl methacrylate, m-methoxyphenylethyl methacrylate, p-methoxyphenylethyl methacrylate and the like; acrylic acid amides such as acrylamide, dimethylaminoethylacrylamide, dimethylaminopropylacrylamide and the like; methacrylic acid amides such as methacrylamide, dimethylaminoethylmethacrylamide,

10 dimethylaminopropylmethacrylamide and the like; cyanoacrylic acid esters; acrolein, cumarone, indene, tetrafluoroethylene, vinyl formal, vinyl formamide and the like, with preference given to ethylene and esters derived from acrylic acid or methacrylic acid such as methyl methacrylate, 2-ethylhexyl

15 acrylate, methyl acrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate and the like.

In addition, a polymerizable unsaturated monomer of the
20 formula (4):



wherein R^7 is hydrogen atom or alkyl group having 1 to 4 carbon atoms; M is metal atom or silicon atom; when M is metal atom, R^8 , R^9 and R^{10} are the same or different and each is organic acid residue, when M is silicon atom, R^8 , R^9 and R^{10} 25 are the same or different and each is alkyl group having 1 to 18 carbon atoms, aryl group or cycloalkyl group; p and q are both 0 when M is divalent metal atom, p is 1 and q is 0 when M is a trivalent metal atom, and both are 1 when M is quatervalent metal atom, is also mentioned. In the above- 30 mentioned formula (4), (meth)acrylic acid metal salt and silyl

(meth)acrylate are preferable, and as M, a metal atom such as zinc, copper and magnesium, and silicon atom are preferable. Examples of the polymerizable unsaturated monomer include the following.

5 Zinc salts of acrylic acid such as zinc acrylate, zinc acrylate benzoate, zinc acrylate propionate, zinc acrylate octylate, zinc acrylate versatate, zinc acrylate stearate, zinc acrylate isostearate, zinc acrylate palmitate, zinc acrylate cresotinate, zinc acrylate α -naphthoate, zinc acrylate β -naphthoate, zinc acrylate monochloroacetate, zinc acrylate monofluoroacetate, zinc acrylate 2,4-dichlorophenoxyacetate, zinc acrylate 2,4,5-trichlorophenoxyacetate, zinc acrylate quinolinecarboxylate, zinc acrylate nitrobenzoate, zinc acrylate nitronaphthalenecarboxylate, zinc acrylate pyruvate
10 and the like;

zinc salts of methacrylic acid such as zinc methacrylate, zinc methacrylate benzoate, zinc methacrylate propionate, zinc methacrylate octylate, zinc methacrylate versatate, zinc methacrylate stearate, zinc methacrylate isostearate, zinc
20 methacrylate palmitate, zinc methacrylate cresotinate, zinc methacrylate α -naphthoate, zinc methacrylate β -naphthoate, zinc methacrylate monochloroacetate, zinc methacrylate monofluoroacetate, zinc methacrylate 2,4-dichlorophenoxyacetate, zinc
25 methacrylate 2,4,5-trichlorophenoxyacetate, zinc methacrylate quinolinecarboxylate, zinc methacrylate nitrobenzoate, zinc methacrylate nitronaphthalenecarboxylate, zinc methacrylate pyruvate and the like;

copper salts of acrylic acid such as copper acrylate, copper acrylate benzoate, copper acrylate propionate, copper
30 acrylate octylate, copper acrylate versatate, copper acrylate stearate, copper acrylate isostearate, copper acrylate palmitate, copper acrylate cresotinate, copper acrylate α -naphthoate, copper acrylate β -naphthoate, copper acrylate monochloroacetate, copper acrylate monofluoroacetate, copper

acrylate 2,4-dichlorophenoxyacetate, copper acrylate 2,4,5-trichlorophenoxyacetate, copper acrylate quinolinecarboxylate, copper acrylate nitrobenzoate, copper acrylate nitronaphthalenecarboxylate, copper acrylate pyruvate and the like;

copper salts of methacrylic acid such as copper methacrylate, copper methacrylate benzoate, copper methacrylate propionate, copper methacrylate octylate, copper methacrylate versatate, copper methacrylate stearate, copper methacrylate 10 isostearate, copper methacrylate palmitate, copper methacrylate cresotinate, copper methacrylate α -naphthoate, copper methacrylate β -naphthoate, copper methacrylate monochloroacetate, copper methacrylate monofluoroacetate, copper methacrylate 2,4-dichlorophenoxyacetate, copper methacrylate 2,4,5- 15 trichlorophenoxyacetate, copper methacrylate quinolinecarboxylate, copper methacrylate nitrobenzoate, copper methacrylate nitronaphthalene carboxylate, copper methacrylate pyruvate and the like;

magnesium salts of acrylic acid such as magnesium
20 acrylate, magnesium acrylate benzoate, magnesium acrylate propionate, magnesium acrylate octylate, magnesium acrylate versatate, magnesium acrylate stearate, magnesium acrylate isostearate, magnesium acrylate palmitate, magnesium acrylate cresotinate, magnesium acrylate α -naphthoate, magnesium
25 acrylate β -naphthoate, magnesium acrylate monochloroacetate, magnesium acrylate monofluoroacetate, magnesium acrylate 2,4-
dichlorophenoxyacetate, magnesium acrylate 2,4,5-
trichlorophenoxyacetate, magnesium acrylate
30 quinolinecarboxylate, magnesium acrylate nitrobenzoate, magnesium acrylate nitronaphthalenecarboxylate, magnesium acrylate pyruvate and the like;

magnesium salts of methacrylic acid such as magnesium methacrylate, magnesium methacrylate benzoate, magnesium methacrylate propionate, magnesium methacrylate octylate,

magnesium methacrylate versatate, magnesium methacrylate stearate, magnesium methacrylate isostearate, magnesium methacrylate palmitate, magnesium methacrylate cresotinate, magnesium methacrylate α -naphthoate, magnesium methacrylate β -naphthoate, magnesium methacrylate monochloroacetate, magnesium methacrylate monofluoroacetate, magnesium methacrylate 2,4-dichlorophenoxyacetate, magnesium methacrylate 2,4,5-trichlorophenoxyacetate, magnesium methacrylate quinolinecarboxylate, magnesium methacrylate nitrobenzoate, magnesium methacrylate nitronaphthalenecarboxylate, magnesium methacrylate pyruvate and the like;

10 silyl acrylates such as trimethylsilyl acrylate, triethylsilyl acrylate, tri-n-propylsilyl acrylate, triisopropylsilyl acrylate, tri-n-butylsilyl acrylate,

15 triisobutylsilyl acrylate, triphenylsilyl acrylate, dimethylbutylsilyl acrylate, dimethylhexylsilyl acrylate, dimethyloctylsilyl acrylate, dimethylcyclohexylsilyl acrylate, dimethylphenylsilyl acrylate, dibutylphenylsilyl acrylate, methyldibutylsilyl acrylate, ethyldibutylsilyl acrylate,

20 dibutylcyclohexylsilyl acrylate, dibutylphenylsilyl acrylate and the like;

25 silyl methacrylates such as trimethylsilyl methacrylate, triethylsilyl methacrylate, tri-n-propylsilyl methacrylate, triisopropylsilyl methacrylate, tri-n-butylsilyl methacrylate,

30 triisobutylsilyl methacrylate, triphenylsilyl methacrylate, dimethylbutylsilyl methacrylate, dimethylhexylsilyl methacrylate, dimethyloctylsilyl methacrylate, dimethylcyclohexylsilyl methacrylate, dibutylphenylsilyl methacrylate, methyldibutylsilyl methacrylate, ethyldibutylsilyl methacrylate, dibutylcyclohexylsilyl methacrylate, dibutylphenylsilyl methacrylate and the like.

Of the above-mentioned examples, preferred are zinc salts of (meth)acrylic acid, copper salts of (meth)acrylic acid

and magnesium salts of (meth)acrylic acid, particularly preferred are zinc salts of (meth)acrylic acid.

The content of the above-mentioned constituting unit derived from a polymerizable unsaturated monomer other than the 5 triphenylboron-containing constituting unit of the formula (1), (2) or (3) is preferably 0-99 wt%, more preferably 5-95 wt%, in the polymer containing triphenylboron (1), (2) or (3) of the present invention. When the content exceeds 99 wt%, the adhesion-preventive effect against aquatic fouling organisms 10 unpreferably becomes insufficient.

The above-mentioned polymerizable unsaturated monomer is introduced during synthesis of a polymer containing a carboxyl group-containing constituting unit of the formula (5) or a polymer containing a constituting unit derived from a 15 vinylpyridine derivative of the formula (10), or during polymerization of a triphenylboron-containing vinyl monomer of the formula [I']. The above-mentioned polymerizable unsaturated monomer may be used alone or in combination of two or more kinds thereof.

20 The polymers containing triphenylboron (1)-(3) of the present invention can be prepared into a fouling preventive such as a fishnet antifouling agent, an underwater antifouling coating (e.g., ship bottom antifouling coating) and the like by a conventional method such as the following methods.

25 A. Fishnet antifouling agent

The fishnet antifouling agent of the present invention shows low toxicity, is highly safe and shows a superior adhesion-preventive effect against coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, Serpula 30 etc.); tubicolous polychaetes (*Hydrodoides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms for a long time.

The fishnet antifouling agent of the present invention is prepared by dispersing or dissolving a polymer containing

triphenylboron (1), (2) or (3) in an organic solvent. The content of the polymer containing triphenylboron (1), (2) or (3) in the fishnet antifouling agent of the present invention can be changed according to the environment of application, 5 which is preferably 1-50 wt%, more preferably 3-25 wt%. When the content is less than 1 wt%, the adhesion-preventive effect against aquatic fouling organisms unpreferably becomes insufficient. Conversely, when it exceeds 50 wt%, the fishnet antifouling agent has a higher viscosity, which unpreferably 10 makes its handling difficult.

The organic solvent to be used for the fishnet antifouling agent of the present invention includes organic solvent of aromatic compound, organic solvent of ketone compound, organic solvent of aliphatic compound and the like. 15 Specific examples include xylene, toluene, pseudocumene, diethylbenzene, triethylbenzene, mesitylene, solvent naphtha, butanol, isopropanol, methyl isobutyl ketone, hexane, propylene glycol monomethyl ether and the like. These solvents may be used alone or in combination of two or more kinds thereof.

20 Where necessary, various resins such as acrylic resin, synthetic rubber, rosin resin, silicone resin, polybutene resin, rubber chloride resin, vinyl chloride resin, alkyd resin, cumarone resin, ethylene-vinyl acetate resin, epoxide resin and the like may be added. These resins may be used alone or in 25 combination of two or more kinds thereof.

When the polymer containing triphenylboron (1), (2) or (3) of the present invention is used as a fishnet antifouling agent, a superior adhesion-preventive effect against aquatic fouling organisms can be achieved even by this polymer alone, 30 but addition of silicone oil, elution regulator, or an antifouling component other than a polymer containing triphenylboron (1), (2) or (3) and the like allows exhibition of a more superior adhesion-preventive effect.

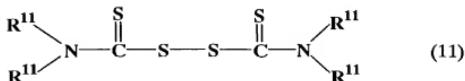
The silicone oil to be used for the fishnet antifouling

agent of the present invention is, for example, dimethylsilicone oil, methyl hydrosilicone oil, (higher) fatty acid modified silicone oil, alkyl modified silicone oil, amino modified silicone oil, epoxy modified silicone oil, polyether modified silicone oil, methylphenylsilicone oil and the like, with preference given to polyether modified silicone oil, higher fatty acid modified silicone oil and the like. These may be used alone or in combination of two or more kinds thereof. While the content of these silicone oils can be 10 optionally varied according to the environment of application, it is preferably 0.1-50 wt%, more preferably 0.5-25 wt%, in a fishnet antifouling agent. When the content is less than 0.1 wt%, an effect afforded by concurrent use is not expected, and when it exceeds 50 wt% conversely, it unpreferably degrades 15 property of a coating film.

The antifouling component other than a polymer containing triphenylboron (1), (2) or (3) to be used for the fishnet antifouling agent of the present invention is exemplified by known antifouling components, such as 1,3-dicyanotetrachlorobenzene, 2-(thiocyanomethylthio)benzothiazole, 20 bis(2-pyridylthio-1-oxide)zinc, bis(2-pyridylthio-1-oxide)copper, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, cuprous oxide, copper thiocyanate (CuSCN), N,N-dimethyldichlorophenyl urea, 4,5-dichloro-2-n- 25 octyl-3-isothiazolone, N-(fluorodichloromethylthio)phthalimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, zinc dimethyldithiocarbamate, bis(dimethyldithiocarbamoyl)zinc ethylene bisdithiocarbamate, 30 pyridine-triphenylboron, triphenylboron-alkyl(3-30 carbon atoms)amine (e.g., triphenylboron-n-octadecylamine, triphenylboron-n-hexadecylamine, triphenylboron-n-octylamine etc.), triphenylboron-rosin amine, copper rhodanide, copper hydroxide, copper naphthenate, manganese ethylene bisdithiocarbamate, zinc ethylene bisdithiocarbamate, N,N'-

dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfide, 3-iodo-2-propynylbutylcarbamate, diiodomethylparatolylsulfane, 2-(4-thiazolyl)-benzoimidazole and the like, and antifouling compounds of other non-tin group.

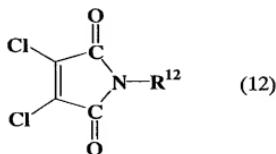
5 There are also mentioned tetraalkyl thiuram disulfides of the formula (11):



wherein each R^{11} is the same or different is alkyl group having 1 to 4 carbon atoms. The alkyl group having 1 to 4 carbon atoms at R^{11} in the formula (11) is exemplified by straight or branched chain alkyl such as methyl, ethyl, n-propyl, isopropyl, butyl and the like, with preference given to ethyl and butyl.

10 Examples of tetraalkyl thiuram disulfides of the formula (11) include tetramethyl thiuram disulfide, tetraethyl thiuram disulfide, tetraisopropyl thiuram disulfide, tetra-n-butyl thiuram disulfide and the like.

15 There are also mentioned 2,3-dichloromaleimides of the formula (12):



wherein R^{12} is hydrogen atom, alkyl group, halogen-substituted 20 alkyl group, cycloalkyl group, phenyl group, alkyl-substituted phenyl group, halogen-substituted phenyl group, benzyl group, alkyl-substituted benzyl group or halogen-substituted benzyl group.

25 The alkyl group at R^{12} of the formula (12) is, for example, straight or branched chain alkyl having 1 to 18 carbon atoms such as methyl, ethyl, isopropyl, n-butyl, t-butyl, octyl,

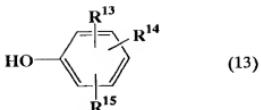
dodecyl, tetradecyl, hexadecyl, octadecyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like.

5 The alkyl-substituted phenyl group is exemplified by dimethylphenyl, diethylphenyl, trimethylphenyl, methylethylphenyl and the like. The halogen-substituted phenyl group is exemplified by dichlorophenyl and the like. The alkyl-substituted benzyl group is exemplified by methylbenzyl, 10 dimethylbenzyl, diethylbenzyl, α -methylbenzyl and the like. The halogen-substituted benzyl group is exemplified by chlorobenzyl, dichlorobenzyl and the like. As R^{12} , ethyl, butyl, diethylphenyl, methylethylphenyl, benzyl are preferable.

Specific examples of 2,3-dichloromaleimides of the

15 formula (12) include 2,3-dichloro-N-ethylmaleimide, 2,3-dichloro-N-isopropylmaleimide, 2,3-dichloro-N-n-butylmaleimide, 2,3-dichloro-N-tert-butylmaleimide, 2,3-dichloro-N-n-octylmaleimide, 2,3-dichloro-N-cyclohexylmaleimide, 2,3-dichloro-N-benzylmaleimide, 2,3-dichloro-N-(2-chlorobenzyl)maleimide, 2,3-dichloro-N-(4-chlorobenzyl)maleimide, 2,3-dichloro-N-(2-methylbenzyl)maleimide, 2,3-dichloro-N-(2,4-dimethylbenzyl)maleimide, 2,3-dichloro-N-(3,4-dimethylbenzyl)maleimide, 2,3-dichloro-N- α -methylbenzylmaleimide, 2,3-dichloro-N-(2,4-dichlorobenzyl)maleimide, 2,3-dichloro-N-(2-ethyl-6-methylphenyl)maleimide, 2,3-dichloro-N-(2,6-dimethylphenyl)maleimide, 2,3-dichloro-N-(2,6-diethylphenyl)maleimide, 2,3-dichloro-N-(2,4-diethylphenyl)maleimide, 2,3-dichloro-N-(2,4,6-trimethylphenyl)maleimide and the like.

There are also mentioned phenols of the formula (13):



wherein R¹³, R¹⁴ and R¹⁵ are the same or different and each is hydrogen atom, alkyl group, halogen-substituted alkyl group, cycloalkyl group, phenyl group, halogen atom, alkoxy group, carboxyl group, alkenyl group or aralkyl group.

In the formula (13), the alkyl group at R¹³, R¹⁴ and R¹⁵ is exemplified by straight or branched chain alkyl having 1 to 9 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, nonyl and the like. The halogen-substituted alkyl group is exemplified by dichloromethyl, dichloroethyl, trichloroethyl and the like. The cycloalkyl group is exemplified by cyclohexyl and the like. The halogen atom is exemplified by fluorine atom, chlorine atom, bromine atom and iodine atom. The alkoxy group is exemplified by straight or branched chain alkoxy having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and the like. The alkenyl group is exemplified by straight or branched chain alkenyl having 2 to 4 carbon atoms such as vinyl, allyl, isopropenyl and the like. The aralkyl group is exemplified by aralkyl having 7 to 9 carbon atoms such as benzyl, cumyl and the like. As R¹³, R¹⁴ and R¹⁵, hydrogen atom, fluorine atom, chlorine atom, methyl, ethyl, t-butyl, nonyl and vinyl are preferable.

Specific examples of phenols of the formula (13) include nonylphenol, cumylphenol, 4,6-ditert-butyl-m-cresol, 1-cyclohexyl-5-methylphenol, 2,6-ditert-butyl-p-cresol, 2-phenylphenol, 2-butyl-6-ethyl-4-isopropylphenol, cyclohexyl-5-methylphenol, 2-bromo-6-chloro-4-dichloromethylphenol, 2-fluoro-4-iodo-3-trichloroethylphenol, 3-hydroxy-5-methoxybenzoic acid, 4-ethoxy-2-vinylphenol and the like.

Preferred antifouling component mentioned above other than the polymer containing triphenylboron (1), (2) or (3)

includes bis(2-pyridylthio-1-oxide)zinc, bis(2-pyridylthio-1-oxide)copper, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, cuprous oxide, copper thiocyanate (CuSCN), N,N-dimethyldichlorophenyl urea, 4,5-dichloro-2-n-5 octyl-3-isothiazolone, N-(fluorodichloromethylthio)phthalimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, zinc dimethyldithiocarbamate, bis(dimethyldithiocarbamoyl)zinc ethylene bisdithiocarbamate, pyridine-triphenylboron, triphenylboron-alkyl(3-30 carbon 10 atoms)amine (e.g., triphenylboron-n-octadecylamine, triphenylboron-n-hexadecylamine, triphenylboron-n-octylamine and the like), triphenylboron-rosin amine, copper rhodanide and tetraethyl thiuram disulfide.

The above-mentioned antifouling component other than the 15 polymer containing triphenylboron (1), (2) or (3) may be used alone or in combination of two or more kinds thereof. The weight ratio of the above-mentioned antifouling component other than the polymer containing triphenylboron (1), (2) or (3) to the polymer containing triphenylboron (1), (2) or (3) of the 20 present invention can be optionally changed according to the environment of application, which is preferably 1:50-50:1, more preferably 1:25-25:1, particularly preferably 1:10-10:1. When the content of the above-mentioned antifouling component is greater than the above-mentioned range, the property of a 25 coating film is degraded and when it is smaller conversely, an effect afforded by concurrent use is not expected.

The elution regulator to be used for the fishnet antifouling agent of the present invention is exemplified by dialkyl polysulfides of the formula (14):



30

wherein each \mathbf{R}^{16} is the same or different and is alkyl group having 1 to 20 carbon atoms and r is an integer of 2-10.

In the formula (14), the alkyl group having 1 to 20 carbon atoms at R^{16} is preferably exemplified by straight or branched chain alkyl having 2 to 19 carbon atoms, such as ethyl, propyl, t-butyl, t-amyl, t-nonyl, t-dodecyl, nonadecyl and the like and r is preferably 3 to 8.

Specific examples of dialkyl polysulfides of the formula (14) include diethyl pentasulfide, dipropyl tetrasulfide, di-tert-butyl disulfide, di-tert-butyl tetrasulfide, di-tert-amyl tetrasulfide, di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, di-tert-dodecyl pentasulfide, dinonadecyl tetrasulfide and the like.

In addition, polybutene having an average molecular weight of 200-1,000, paraffins, petrolatum, glycerin, polyhydric alcohols and fatty acid esters can be used as an elution regulator.

Examples of polybutene having an average molecular weight of 200-1,000 include LV-5, LV-10, LV-25, LV-50, LV-100, HV-15, HV-35, HV-50, HV-100, HV-300 manufactured by NIPPON OIL COMPANY, LTD. and the like. Examples of paraffins include liquid paraffin, paraffin wax, paraffin chloride and the like. Examples of petrolatum include white petrolatum, yellow petrolatum and the like.

Preferable examples of the above-mentioned elution regulator include di-tert-nonyl pentasulfide, di-tert-octyl pentasulfide, polybutene, liquid paraffin, white petrolatum and yellow petrolatum.

The above-mentioned elution regulator may be used alone or in combination of two or more thereof. The content of the above-mentioned elution regulator can be optionally changed according to the environment of application, which is preferably 1-30 wt%, more preferably 3-20 wt%, particularly preferably 5-10 wt%, in a fishnet antifouling agent. When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 30 wt%, it

unpreferably degrades property of a coating film.

B. Underwater antifouling coating

The underwater antifouling coating of the present invention shows low toxicity, is highly safe and shows a superior adhesion-preventive effect against coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, Serpula etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios kraussii*, *Dexiospira spirillum* etc.); and other aquatic fouling organisms for a long time.

The underwater antifouling coating of the present invention can be prepared by adding a polymer containing triphenylboron (1), (2) or (3) in water-soluble resin or non-water-soluble resin, and mixing and dispersing them using a paint conditioner, homomixer and the like. In addition, an additive such as other component generally used for coating, solvent (xylene, methyl isobutyl ketone, n-butanol, butyl acetate etc.), pigment (red iron oxide, titanium oxide, zinc oxide etc.), plasticizer, filler (talc, fine silica etc.), curing promoter and the like can be mixed as necessary.

The content of the polymer containing triphenylboron (1), (2) or (3) in the underwater antifouling coating of the present invention can be optionally changed according to the environment of application, which is preferably 1 wt% - 80 wt%, more preferably 3 wt% - 40 wt%. When the content is less than 1 wt%, an adhesion-preventive effect against aquatic fouling organisms becomes insufficient, and conversely, when it exceeds 80 wt%, it increases the viscosity of the coating, which unpreferably makes handling difficult.

When the polymer containing triphenylboron (1), (2) or (3) of the present invention is used as an underwater antifouling agent, a superior adhesion-preventive effect against aquatic fouling organisms can be achieved even by this polymer alone, but addition of silicone oil, elution regulator,

an antifouling component other than a polymer containing triphenylboron (1), (2) or (3) and the like allow exhibition of a more superior adhesion-preventive effect. Silicone oil, elution regulator, the antifouling components other than a 5 polymer containing triphenylboron (1), (2) or (3) and the like include those exemplified for fishnet antifouling agent. Where necessary, various resins explained with regard to the fishnet antifouling agent can be also added.

The content of the silicone oil can be optionally 10 changed according to the environment of application, which is preferably 0.1 - 50 wt%, more preferably 0.5 - 25 wt%, in an underwater antifouling coating. When the content is less than 0.1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 50 wt%, it unpreferably 15 degrades property of a coating film.

The weight ratio of the antifouling component other than the polymer containing triphenylboron (1), (2) or (3) to the polymer containing triphenylboron (1), (2) or (3) of the present invention can be optionally changed according to the 20 environment of application, which is preferably 1:50 - 50:1, more preferably 1:25 - 25:1, particularly preferably 1:10 - 10:1. When the above-mentioned antifouling component is greater than the above-mentioned range, the property of a 25 coating film is degraded, and conversely, when it is lower, an effect afforded by concurrent use is not expected undesirably.

The content of the elution regulator can be optionally changed according to the environment of application, which is preferably 1 - 30 wt%, more preferably 3 - 20 wt%, particularly preferably 5-10 wt%, in an underwater antifouling coating. 30 When the content is less than 1 wt%, an effect afforded by concurrent use is not expected, and conversely, when it exceeds 30 wt%, it unpreferably degrades property of a coating film.

Examples

The present invention is explained in detail in the

following by way of Examples and Comparative Examples. It is needless to say that the present invention is not limited by these Examples. In the Examples, the contents are in wt%. In the Tables, triphenylboron is abbreviated as TPB.

5 Example 1 <synthesis of triphenylboron adduct>

Into a four neck 1 L flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed an aqueous solution of sodium hydroxide adduct of triphenylboron (250.3 g, 9% aqueous solution, manufactured by 10 Tokyo Kasei Co., Ltd.) and stirring was started. Ethylene diamine (4.81 g, manufactured by Tosoh Corporation) was dropwise added at room temperature from the dropping funnel. After the dropwise addition, the mixture was stirred at the same temperature for 5 hr. The precipitate was collected by 15 filtration and washed with water and dried to give white powdery substance (21.64 g). The obtained compound was subjected to elemental analysis and IR (infrared) spectrum analysis. As a result, the compound was confirmed to be a triphenylboron-ethylenediamine adduct (triphenylboron adduct A) 20 of the objective substance, m.p. 157.8-159.8°C.

Examples 2-4 <synthesis of triphenylboron adduct>

By synthesizing in the same manner as in Example 1 using the starting materials shown in Table 1, triphenylboron adducts B-D were obtained. They are shown in Table 1 together 25 with triphenylboron adduct A. In Table 1, each figure is in g (gram).

Table 1 triphenylboron adduct

(unit:g)

amine		Example			
		1	2	3	4
	Ethylenediamine	4.81			
	Propylenediamine		5.93		
	p-phenylene-diamine			8.65	
	4-aminopyridine				7.53
	TPB·NaOH adduct *1	250.3	250.3	250.3	250.3
	Yield	21.64	21.38	24.21	24.28
	Adduct reference	A	B	C	D

*1: sodium hydroxide adduct of triphenylboron, 9% aqueous solution

5

Example 5 <synthesis of polymers containing triphenylboron (1)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a solution (100 g) of methacrylic acid/methyl 10 methacrylate/2-ethylhexyl acrylate copolymer (resin 1, M_w =ca 10,000, acid value 18.6 mg KOH/g) in 40% xylene/n-BuOH, and stirring was initiated. The triphenylboron-ethylenediamine adduct (triphenylboron adduct A, 10.1 g) synthesized in Example 1 was cast in at room temperature and then xylene (16.1 g) was 15 added. The mixture was stirred at the same temperature for 5 hr to give a solution (polymer solution A, 126 g) of a polymer containing triphenylboron in xylene. The solvent was evaporated under reduced pressure from a part of the xylene solution and the residue was dried to give a pale-yellow white 20 resin like substance. By IR (infrared) spectrum analysis, it was confirmed to be the objective substance. The weight average molecular weight was about 13,000 (GPC). The IR (infrared) spectrum of this polymer is shown in Fig. 1.

Examples 6-15 <synthesis of polymers containing triphenylboron

25 (1) and (2)>

In the same manner as in Example 5 using a triphenylboron adduct, a carboxyl group-containing polymer and a solvent shown

in Table 2, solutions of polymer containing a triphenylboron (polymer solutions B-K) were synthesized. They are collectively shown in Table 2 together with the polymer solution A. Unless particularly indicated, each figure in Table 2 is in g (gram).

Table 2 polymer containing triphenylboron
(unit: g unless specifically indicated)

TPB	Example										
	5	6	7	8	9	10	11	12	13	14	15
adduct A	10.1	12.6	10.5	16.1	10.5						
adduct B						11.9	13.2				
adduct C								11.6	14.6		
adduct D										11.2	14.0
carboxyl group-containing polymer	100.0					100.0	100.0			100.0	
Resin 1											
Resin 2		20.0					20.0		20.0		20.0
Resin 3			20.0								
Resin 4				20.0							
Resin 5					50.0						
solvent	16.1	48.9	45.8	54.2	90.8	18.9	49.7	18.4	51.9	17.8	51.0
Yield (g)	126.0	81.2	76.0	90.0	151.0	130.3	82.4	130.0	86.2	129.0	86.0
heating residue (%)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
weight average molecular weight ($\times 10^4$)	1.3	1.6	1.8	8.2	1.4	1.4	1.7	1.5	1.7	1.4	1.7
basic constituting unit (%)	25.6	47.7	44.1	57.1	21.5	26.2	47.4	27.9	50.9	27.2	50.0
TPB content (%)	16.1	30.9	27.7	35.8	13.9	15.9	29.6	15.6	29.2	15.7	29.7
polymer solution reference	A	B	C	D	E	F	G	H	I	J	K

Resin 1: methacrylic acid/methyl acrylate/2-ethylhexyl acrylate copolymer (solid content 40%, acid value 18.6 mg KOH/g)
 Resin 2: ethylene/acrylic acid (15 wt%) copolymer
 Resin 3: ethylene/methacrylic acid (15 wt%) copolymer
 Resin 4: t-butyl acrylate/ethyl acrylate/methacrylic acid (23 wt%) copolymer
 Resin 5: ethylene acrylic acid (10 wt%), about 50% Zn salt) copolymer
 solvent: xylene alone or xylene/nBuOH mixed system

Examples 16-29 and Comparative Examples 1-3 <FormulationExamples of fishnet antifouling agents>

The fishnet antifouling agents of the present invention (Examples 16-29) were prepared in the compositions shown in Table 3 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, fishnet antifouling agents of Comparative Examples 1-3 were prepared. Each figure in Table 3 is in wt%.

Table 3 fishnet antifouling agent

Compo- nent	Composition (wt%)									Comparative Example		
	Example									1	2	3
Poly- mer solu- tion	16	17	18	19	20	21	22	23	24	25	26	27
A	51.6	51.6	51.6	51.6								
B					26.8							
C						30.0						
D							23.2					
E								59.6				
F									52.1			
G										28.0		
H											53.2	
I												28.4
J												52.8
K												27.9
TET												10.0
PK												10.0
TNPS												5.0
LV-50												5.0
LR-155												5.0
silicone oil	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
xylene	48.4	44.4	39.4	34.4	64.2	61.1	67.9	31.4	38.9	63.0	37.8	62.6

TET: tetraethyl thiuram disulfide

PK: triphenylboron-pyridine adduct

TNPS: di-t-nonyl polysulfide (maximum value of occupation 5)

LV-50: polybutene (Nippon Petrochemicals Co., Ltd.)

LR-155: acrylic resin (50% xylene solution, Mitsubishi Rayon Co., Ltd.)

silicone oil: polyether modified silicone oil

Examples 30-44 and Comparative Examples 4-7 <FormulationExamples of ship bottom antifouling coatings>

The ship bottom antifouling coating of the present invention (Examples 30-44) were prepared in the compositions shown in Table 4 using the polymer solutions A-K obtained in Examples 5-15. In the same manner, ship bottom antifouling coatings of Comparative Examples 4-7 were prepared. Each figure in Table 4 is in wt%.

Table 4 ship bottom antifouling coating

	component	Coating composition (wt%)							Comparative Example											
		30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	4	5	6	7
polymer solution	A	50	50																	
	B		50																	
	C			50																
	D				50															
	E					50														
	F						50	50												
	G								50											
	H									50	50									
pigment	I											50	50							
	J													50	50					
	K															50				
	zinc oxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	red oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	colloidal silica	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	talc	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	cuprous oxide	10																		
polluting component	PK																			
	TPB-8																			
	vinylic resin varnish																			
	chlorinated isoprene rubber																			
	xylene	15	5	15	15	15	15	5	15	15	5	15	15	5	15	15	10	15	10	10
	MBK	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	BuOH	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

PK: triphenylboron-pyridine adduct, MBK: methyl isobutyl ketone
 TPB-8: triphenylboron-n-octylamine adduct, BuOH: n-butanol

Experimental Example 1 <fishnet antifouling agent effect test>

The fishnet antifouling agents of Examples 16-29 and Comparative Examples 1-3 were respectively applied to polyethylene unknotted nets (6 knot, 400 denier/60 yarns) by immersion, air-dried and set on a metal frame. The test nets were retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken and the degree of fouling due to adhesion of aquatic fouling organisms was observed. The degree of fouling was evaluated according to the following criteria, 10 the results of which are shown in Table 5.

Table 5 fishnet antifouling agent effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	16	A	A	A	A	B	B
	17	A	A	A	A	A	A
	18	A	A	A	A	A	A
	19	A	A	A	A	A	A
	20	A	A	A	A	A	A
	21	A	A	A	A	A	A
	22	A	A	A	A	A	A
	23	A	A	A	A	A	A
	24	A	A	A	A	A	A
	25	A	A	A	A	A	A
	26	A	A	A	A	A	A
	27	A	A	A	A	A	A
	28	A	A	A	A	A	A
	29	A	A	A	A	A	A
Comparative Example	1	C	D				
	2	A	A	A	B	C	D
	3	D					
untreated		D					

untreated: polyethylene unknotted net not treated with fishnet antifouling agent

15 Evaluation criteria of degree of fouling of net

Evaluation A: Area of fouling of fishnet, 0%, no adhesion of aquatic fouling organisms.

Evaluation B: Area of fouling of fishnet, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

Evaluation C: Area of fouling of fishnet, 10% to less than 50%, great amount of adhesion of aquatic fouling organisms, unpractical as a fishnet.

Evaluation D: Area of fouling of fishnet, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms.

A number of aquatic fouling organisms such as barnacle and *Hydroides norvegica* adhered to the nets of Comparative Examples 1-3 and untreated nets in 1 to 4 months. On the other hand, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the nets of Examples 16-29 retained underwater for at least 4 months.

Experimental Example 2 <ship bottom antifouling coating effect test>

The ship bottom antifouling coatings of Examples 30-44 and Comparative Examples 4-7 were applied on both sides of 50×100×2 mm hard vinyl chloride plates to achieve a dry film thickness of about 100 micron. After air-drying for one day, these test plates were retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken and the degree of fouling of the test plates due to adhesion of aquatic organisms was observed. The degree of fouling was evaluated according to the following criteria, the results of which are shown in Table 6.

25

Table 6 ship bottom antifouling coating effect test results

		1 month	2 month	3 month	4 month	5 month	6 month
Example	30	A	A	A	A	A	A
	31	A	A	A	A	A	A
	32	A	A	A	A	A	A
	33	A	A	A	A	A	A
	34	A	A	A	A	A	A
	35	A	A	A	A	A	A
	36	A	A	A	A	A	A
	37	A	A	A	A	A	A
	38	A	A	A	A	A	A
	39	A	A	A	A	A	A
	40	A	A	A	A	A	A
	41	A	A	A	A	A	A
	42	A	A	A	A	A	A
	43	A	A	A	A	A	A
	44	A	A	A	A	A	A
Comparative Example	4	A	A	A	B	B	C
	5	A	B	C	C	D	
	6	A	B	B	C	D	
	7	A	B	C	D		
untreated		D					

untreated: hard vinyl chloride plates not treated with ship bottom antifouling coating

5 Evaluation criteria of degree of fouling of test plate

Evaluation A: Area of fouling of test plate, 0%, no adhesion of aquatic fouling organisms.

Evaluation B: Area of fouling of test plate, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

Evaluation C: Area of fouling of test plate, 10% to less than 50%, great amount of adhesion of aquatic fouling organisms, impractical as a ship bottom antifouling coating.

Evaluation D: Area of fouling of test plate, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms.

A number of aquatic fouling organisms such as barnacle

and *Hydrodoides norvegica* adhered to the plates of Comparative Examples 4-7 and untreated plates in 1 to 4 months. On the other hand, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the plates of Examples 30-44 retained underwater for 6 months.

Example 45 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed poly(4-vinylpyridine) (5.3 g, reagent of Aldrich, molecular weight about 60,000) dissolved in methanol (50 g) and stirring was started. The temperature of the system was raised to 50°C, an aqueous solution (157 g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was added dropwise from the dropping funnel over about 1 hr. After the completion of the dropwise addition, the mixture was stirred at the same temperature for 1 hr. The solvent was evaporated under reduced pressure and water was added. The precipitated viscous insoluble material was collected by filtration, washed with water and dried to give 14 g of a pale-yellowish white polymer substance (polymer A).

The obtained compound was subjected to IR (infrared) spectrum analysis. As a result, the compound was confirmed to be the objective substance. The IR (infrared) spectrum thereof is shown in Fig. 2. In addition, the weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 198,000. The content of triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer A were 85 wt% and 59 wt%, respectively.

Example 46 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed 4-vinylpyridine-butyl methacrylate copolymer (5.3 g, reagent of Aldrich, butyl methacrylate content 10 wt%)

dissolved in methanol (50 g) and stirring was started. The temperature of the system was raised to 50°C, an aqueous solution (142, g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was 5 added dropwise from the dropping funnel over about 1 hr. After the completion of the dropwise addition, the mixture was stirred at the same temperature for 1 hr. The solvent was evaporated under reduced pressure and water was added. The precipitated viscous insoluble material was collected by 10 filtration, washed with water and dried to give 12.3 g of a pale-yellowish white polymer substance (polymer B). The content of triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer B were 78 wt% and 54 wt%, respectively.

15 Example 47 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a 49 wt% xylene solution (28.3 g) of 4-vinylpyridine-butyl methacrylate copolymer (4-vinylpyridine content 10 wt%) 20 and stirring was started. The temperature of the system was raised to 50°C, and an aqueous solution (37.0 g, reagent of Tokyo Kasei Co., Ltd.; 9% aqueous solution) of sodium hydroxide adduct of triphenylboron was added dropwise from the dropping funnel over about 30 min. After the completion of the 25 dropwise addition, the mixture was stirred at the same temperature for 2 hr. The reaction mixture was transferred to a partition funnel and left standing. The aqueous layer was partitioned and water was added to the xylene layer and washed. Washing was repeated until the partitioned aqueous layer did 30 not show alkalinity, and the solvent was evaporated under reduced pressure to give 15.5 g of a yellow-brown resin-like substance (polymer C). The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 140,000. The content of the triphenylboron-containing

constituting unit of the formula (3) and the content of triphenylboron in polymer C were 14.3 wt% and 10.0 wt%, respectively.

Example 48 <synthesis of polymer containing triphenylboron (3)>

5 Into a four neck 300 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was placed a 45 wt% xylene solution (46.7 g) of 4-vinylpyridine-zinc methacrylate copolymer (4-vinylpyridine content 5 wt%) and stirring was started. The temperature of the system was
10 raised to 50°C, and triphenylboron (2.5 g, reagent of Aldrich) was added by small portions. After the completion of the addition, the mixture was stirred at the same temperature for 2 hr. The solvent was evaporated under reduced pressure to give 21.0 g of a yellow-brown resin-like substance (polymer D).
15 The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 3,000. The content of the triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in polymer D were 11.8 wt% and 8.2 wt%, respectively.

20 Examples 49-52 and Comparative Examples 8-9 <Formulation

Example of fishnet antifouling agent>

The fishnet antifouling agents of the present invention (Examples 49-52) were prepared in the compositions shown in Table 7 using the polymers A-D obtained in Examples 45-48. In
25 the same manner, fishnet antifouling agents of Comparative Examples 8-9 were prepared. Each figure in Table 7 is in wt%. The polybutene used was LV-50 (manufactured by Nippon Petrochemicals Co., Ltd.), and the acrylic resin (50% xylene solution) was LR-155 (manufactured by Mitsubishi Rayon Co.,
30 Ltd.).

Table 7 fishnet antifouling agent

(unit: wt%)

component	Example 49	Example 50	Example 51	Example 52	Comparative Example 8	Comparative Example 9
polymer A	10					
polymer B		10				
polymer C			30			
polymer D				30		
acrylic resin (50% xylene solution)	20	20			20	20
xylene	70	70	70	70	60	60
pyridine-triphenyl-boron						10
tetraethyl-thiuram disulfide					10	
polybutene					5	5
yellow petrolatum					5	5

5 Experimental Example 3 <fishnet antifouling agent effect test>

The fishnet antifouling agents of Examples 49-52 and Comparative Examples 8-9 were respectively applied to polyethylene unknotted nets (6 knots, 400 denier/60 yarnts) by immersion, air-dried and retained at about 1.5 meters underwater in the sea off Shukumo-shi, Kochi-ken, for 6 months from April 1998. The nets were pulled out every month and the degree of fouling was evaluated for 6 months according to the following criteria, the results of which are shown in Table 8.

10 Evaluation criteria of degree of fouling of net

15 Evaluation A: Area of fouling of fishnet, 0%, no adhesion of aquatic fouling organisms.

Evaluation B: Area of fouling of fishnet, over 0% to less than 10%, small amount of adhesion of aquatic fouling organisms to the extent practically acceptable.

20 Evaluation C: Area of fouling of fishnet, 10% to less than 50%,

great amount of adhesion of aquatic fouling organisms, often unusable as a fishnet.

Evaluation D: Area of fouling of fishnet, 50% or more, markedly greater amount of adhesion of aquatic fouling organisms, unusable as fishnet.

5

Table 8 fishnet antifouling agent effect test results

	1 month	2 month	3 month	4 month	5 month	6 month
Example 49	A	A	A	A	B	B
Example 50	A	A	A	A	B	B
Example 51	A	A	A	A	B	B
Example 52	A	A	A	A	A	A
Comparative Example 8	C	D				
Comparative Example 9	A	A	A	B	C	C
untreated net	D					

untreated net: polyethylene unknotted net not treated with fishnet antifouling agent

10 A number of aquatic fouling organisms such as barnacle and *Hydroides norvegica* adhered to the nets of Comparative Example 8 and untreated nets in 1 to 2 months. while adhesion of aquatic fouling organisms to the net of Comparative Example 9 was not found in 3 months, they started to adhere in 4 months.

15 In contrast, shellfish, tubicolous polychaetes or other aquatic fouling organisms did not adhere at all to the nets of Examples 49-52 retained underwater for 4 months.

Examples 53-64 and Comparative Examples 10-15 <Formulation Example of underwater antifouling coating>

20 The underwater antifouling coating (Examples 53-64 and Comparative Examples 10-15) were prepared in the compositions shown in Table 9 by mixing each component.

Table 9 underwater antifouling coating

Compo- nents	Compo- nent	Coating composition (wt%)													Comparative Example				
		Example																	
resin	viny- l resin	53	54	55	56	57	58	59	60	61	62	63	64	10	11	12	13	14	15
	chlori- nated isoprene rubber	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
pigment	zinc oxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	red oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
colloid silica	colloid silica	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	talc	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
anti- fouling active ingre- dient	polymer A	10	5	5															
	polymer B				10	5	5												
PK	anti- polymer C							10	5	5									
	polymer D										10	5	5						
TPB-8	TPB-8													10	5	5	10	5	5
	cuprous oxide											10		10			10		
organic solvent	copper rhodanide												10		10			10	
	xylene	15	10	10	15	10	10	15	10	10	15	10	10	10	10	10	10	10	10
organic solvent	MIBK	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	n-butyl alcohol	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

PK: pyridine-triphenylboron, TPB-8: triphenylboron-n-octylamine, MIBK: methyl isobutyl ketone

Experimental Example 4 <underwater antifouling coating effect test>

A typical anticorrosive coating was applied to sandblasted steel plates in advance, and the coatings of Examples 53-64 and Comparative Examples 10-15 were applied twice with a brush on the dry film to prepare test plates (100 mm × 300 mm) having an underwater antifouling coating having a dry coating film thickness of about 100 µm. These test plates were retained at about 1.5 meters underwater in the Shukumo gulf, Shukumo-shi, Kochi-ken, for 12 months, and the degree of adhesion of aquatic fouling organisms was observed every 3 months during this period. The degree of adhesion of the aquatic fouling organisms was evaluated according to the following criteria, the results of which are shown in Table 10.

15 Evaluation criteria of degree of adhesion of aquatic fouling organisms

No adhesion of aquatic fouling organisms ◎
Area of adhesion of aquatic fouling organisms
 less than 10% ○
20 Area of adhesion of aquatic fouling organisms
 10% - less than 20% △
 Area of adhesion of aquatic fouling organisms
 20% - less than 30% ×
 Area of adhesion of aquatic fouling organisms
25 30% or above ××

Table 10 underwater antifouling coating effect test results

	adhesion-preventive effect			
	3 month	6 month	9 month	12 month
Example 53	◎	◎	◎	◎
Example 54	◎	◎	◎	◎
Example 55	◎	◎	◎	◎
Example 56	◎	◎	◎	◎
Example 57	◎	◎	◎	◎
Example 58	◎	◎	◎	◎
Example 59	◎	◎	◎	◎
Example 60	◎	◎	◎	◎
Example 61	◎	◎	◎	◎
Example 62	◎	◎	◎	◎
Example 63	◎	◎	◎	◎
Example 64	◎	◎	◎	◎
Comparative Example 10	◎	◎	○	○
Comparative Example 11	△	×	××	××
Comparative Example 12	△	×	××	××
Comparative Example 13	◎	◎	○	○
Comparative Example 14	△	×	××	××
Comparative Example 15	△	×	××	××

As is evident from Table 10, the test plates coated with the coatings of Comparative Examples 10-15 showed a decreased adhesion-preventive effect in 3-9 months of immersion. In contrast, the test plates coated with the coatings of Examples 53-64 did not show adhesion of aquatic fouling organisms even after 12 months of immersion in sea.

Example 65 <synthesis of triphenylboron-containing vinyl monomer>

Into a four neck 500 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer was

placed an aqueous solution (370 g, 9% aqueous solution, reagent of Tokyo Kasei Co., Ltd.) of sodium hydroxide adduct of triphenylboron and stirring was started at room temperature. Thereto was dropwise added 4-vinylpyridine (10.5 g, Koei Chemical co., Ltd.) over about 30 minutes. After the dropwise addition, the mixture was stirred at the same temperature for 2 hr. The precipitate white insoluble material was collected by filtration, washed with water and dried to give a white powder (34.9 g). The obtained compound was subjected to IR (infrared) spectrum analysis. As a result, the compound was confirmed to be a 4-vinylpyridine-triphenylboron adduct.

Example 66 <synthesis of polymer containing triphenylboron (3)>

Into a four neck 500 mL flask equipped with a mechanical stirrer, a condenser, a dropping funnel and a thermometer were placed a triphenylboron-containing vinyl monomer (10 g) synthesized in Example 65, butyl methacrylate (90 g), xylene (100 g) and azobisisobutyronitrile (0.2 g), and the mixture was polymerized for 2 hr under a nitrogen atmosphere while maintaining the temperature at 80-90°C. Azobisisobutyronitrile (0.2 g) was further added at the same temperature and the mixture was polymerized for 2 more hours to give a polymer solution having a heating residue of 50.1%. The weight average molecular weight was measured by gel permeation chromatography (GPC) and found to be about 20,000. The content of the triphenylboron-containing constituting unit of the formula (3) and the content of triphenylboron in the obtained polymer were 9.7 wt% and 6.9 wt%, respectively.

Industrial Applicability

As is evident from the foregoing explanation, the polymer containing triphenylboron (1), (2) or (3) of the present invention shows extremely small adhesion of coelenterates (hydrozoas, obelia etc.); shellfish (barnacle, blue mussel, oyster, Serpula etc.); tubicolous polychaetes (*Hydroides norvegica*, *Serpula vermicularis*, *Pomatoleios*

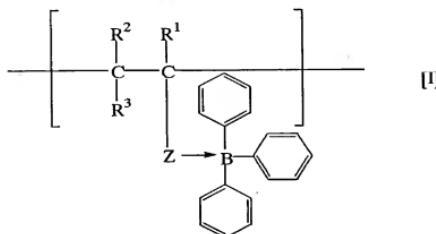
kraussii, *Dexiospira spirillum* etc.); and other aquatic fouling organisms and shows a superior adhesion-preventive effect for a long time. Because it has a function of not only an active ingredient but also a binder, the polymer characteristically 5 shows fine miscibility with other coating resins and a less adverse influence on the environment. Therefore, a fouling preventive containing this polymer, such as a fishnet antifouling agent and an underwater antifouling coating (e.g., a ship bottom antifouling coating etc.), becomes extremely 10 useful.

This application is based on patent application Nos. 1999-206799, 2000-76939 and 2000-80153 filed in Japan, the contents of which are hereby incorporated by reference.

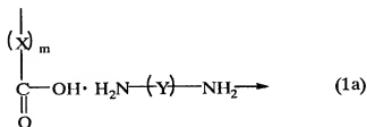
15

WHAT IS CLAIMED IS

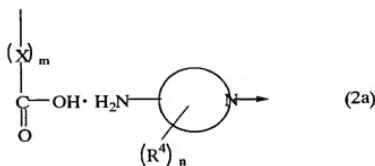
1. A polymer comprising a triphenylboron-containing constituting unit of the formula [I]:



5 wherein R¹, R² and R³ are the same or different and each is hydrogen atom or alkyl group having 1 to 4 carbon atoms;
 Z is a group of the formula (1a):



10 , the formula (2a):



or the formula (3a):



(3a)

wherein, in the formulas (1a) and (2a), X is alkylene group having 1 to 18 carbon atoms, arylene group, aralkylene group, $-C(=O)-$ group, $-C(=O)-R^5-$ group, $-C(=O)-O-R^5-$ group, $-O-R^5-$ group, $-C(=O)-O-R^5-O-C(=O)-$ group or $-C(=O)-O-R^5-O-C(=O)-R^6-$ group (where R^5 and R^6 are the same or different and each is alkylene group having 1 to 18 carbon atoms or arylene group); Y is alkylene group having 2 to 18 carbon atoms, arylene group, aralkylene group or cycloalkylene group; m is 0 or 1; R^4 in the number of n are the same or different and each is halogen atom or alkyl group having 1 to 18 carbon atoms; n is an integer of 0-3; and a group of the formula (2b):



(2b)

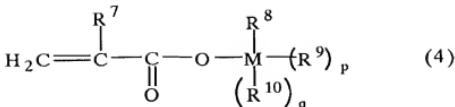
is amino-substituted, N-containing heterocycle.

2. The polymer of claim 1, wherein the weight average molecular weight is 1,000-1,000,000.

3. The polymer of claim 1, which further comprises a constituting unit derived from a polymerizable unsaturated monomer other than a constituting unit of the formula [I].

25

4. The polymer of claim 3, wherein the polymerizable unsaturated monomer has the formula (4):



wherein R⁷ is hydrogen atom or alkyl group having 1 to 4 carbon atoms; M is metal atom or silicon atom; when M is metal atom, R⁸, R⁹ and R¹⁰ are the same or different and each is organic acid residue, when M is silicon atom, R⁸, R⁹ and R¹⁰ are the same or different and each is alkyl group having 1 to 18 carbon atoms, aryl group or cycloalkyl group; when M is divalent metal atom, p and q are both 0, when M is trivalent metal atom, p is 1 and q is 0, and when M is quattrevalent metal atom, both are 1.

10

5. The polymer of claim 4, wherein, in the formula [I], when Z is a group of the formula (3a), R⁷ is hydrogen atom or methyl group, and M is metal atom.

16

6. The polymer of claim 4 or 5, wherein the metal atom is zinc, copper or magnesium.

7. A composition comprising the polymer of any of claims 1-6.

2

8. The composition of claim 7, further comprising at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling component other than the polymer of claim 1.

25

9. A fouling preventive comprising the polymer of any of claims 1-6.

10. The fouling preventive of claim 9, which further comprises at least one member selected from the group consisting of silicone oil, an elution regulator and an antifouling

component other than the polymer of claim 1.

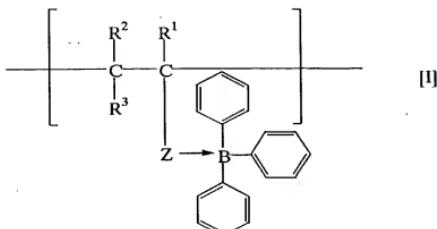
11. The fouling preventive of claim 9 or 10, which is for preventing fouling of a fishnet.

5

12. The fouling preventive of claim 9 or 10, which is for an underwater antifouling coating.

Abstract of the Disclosure

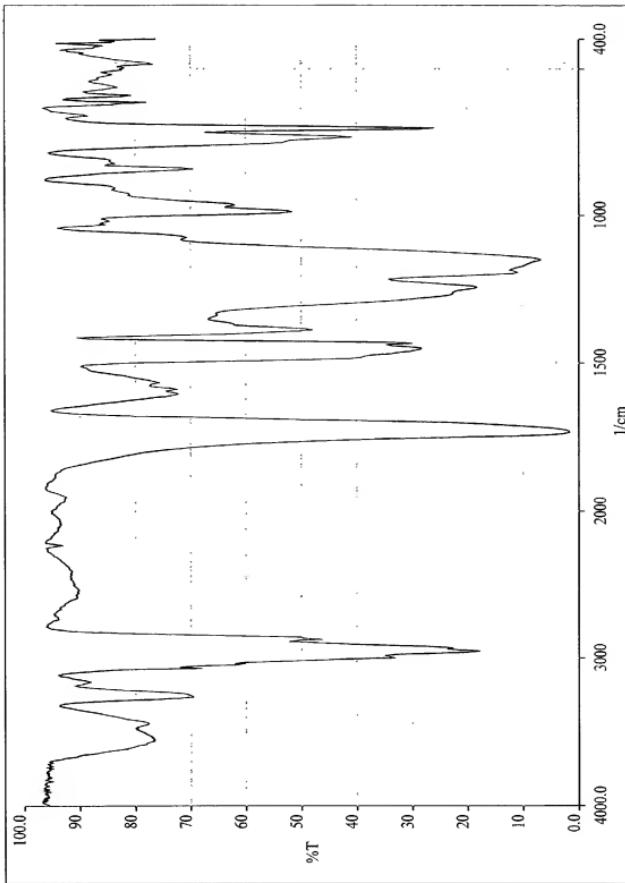
A polymer containing a triphenylboron-containing constituting unit of the formula [I]:



5 wherein each symbol is as defined in the specification, shows a superior adhesion-preventive effect against aquatic fouling organisms, such as coelenterates, shellfish, tubicolous polychaetes and the like, for a long time, shows a function of not only an active ingredient but also a binder, the polymer 10 characteristically shows fine miscibility with other coating resins and a less adverse influence on the environment. Therefore, it can be used as a superior preventive of fouling due to the adhesion of aquatic fouling organisms.

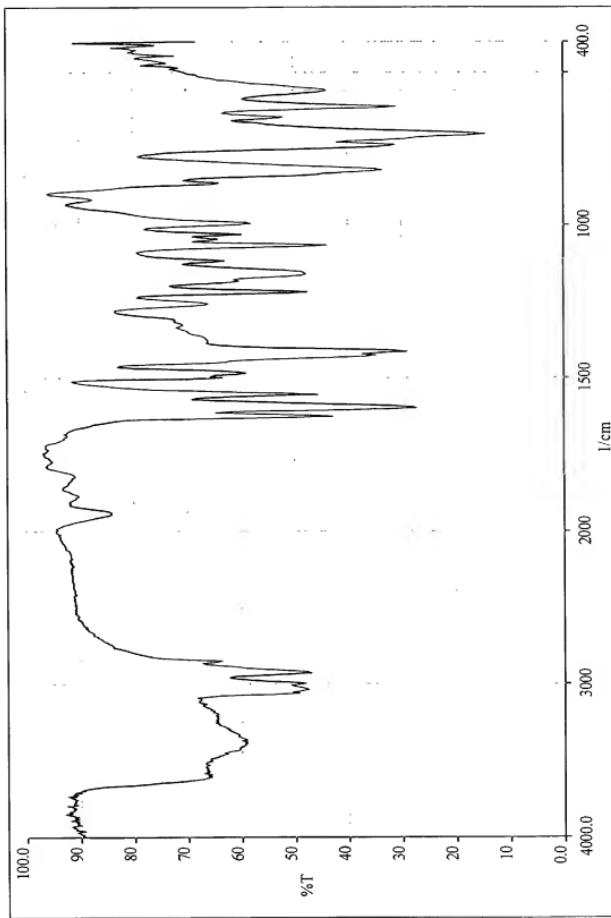
1990316 10 10/031618

FIG. 1



100031618 1021302 107031618

FIG. 2



DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

米国特許出願宣言書及び委任状

Japanese Language Declaration
日本語宣言書（英語でご記入下さい）

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

下記の氏名の発明者として、私は以下の通り宣言します。私の住所、郵便物送付先、国籍は下記の私の氏名の後に記載された通りです。下記の名称の発明に關して請求の範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の氏名が複数の場合）であると信じています。

Title (発明の名称) :

POLYMER CONTAINING TRIPHENYLBORON AND USE THEREOF

, of which is described and claimed in:

上記名称の発明を記述し特許請求する書類は、以下のいずれかです。

() the attached specification, or

本状に添付した明細書

() the specification in the application Serial No. _____, filed _____;

（上記日付） 提出の米国出願番号（上記出願番号）で、

and with amendments through _____ (if applicable), or

（該当する場合）（上記日付等）に訂正された明細書

(X) the specification in International Application No. PCT/JP00/04888, filed on July 21, 2000,

and as amended on _____ (if applicable).

（上記日付） 提出の特許協力条約に基づく国際出願番号PCT/（上記出願番号）で、

（該当する場合）（上記日付等）に訂正された明細書

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

私は、特許請求の範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許性の有無について重要な情報を開示する義務があることを認めます。

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

私は、米国法典第35編119条（もし本願が意匠に関する出願の場合は172条）に基き、下記の特許出願又は発明者証の出願についての優先権の利益をここに主張するとともに、優先権主張の基礎となる出願日を有する、本出願の前に出願された特許または発明者証の出願を以下にすべて、枠内をマークすることで示しています。

COUNTRY 国名	APPLICATION NO. 出願番号	DATE OF FILING 出願日	PRIORITY CLAIMED 優先権主張
Japan	206799/1999	July 21, 1999	Yes
Japan	76939/2000	March 17, 2000	Yes
Japan	80153/2000	March 22, 2000	Yes

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or 365(c) of any PCT international application designating the United States listed below, and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which become available between the filing date of the prior application and the national or PCT international filing date of this application:

私は、米国法典第35編120条に基いて下記の米国特許出願、又は米国を指定している特許協力条約365条(c)に基づく優先権をここに主張します。また、本出願の各請求の範囲の技術的事項が米国法典第35編112条第1段で規定された方法で先行する米国特許出願に開示されない限り、当該先行出願の出願日以降で本出願の国内又はPCTに基づく国際出願の提出日までの期間中に入手できるようになった、連邦規則法典第37編1条56項で定義された特許性の有無に関する重要な情報について、開示義務があることを認識しています。

APPLICATION SERIAL NO. 出願番号	U.S. FILING DATE 米国出願日	STATUS: PATENTED, PENDING, ABANDONED 現状:特許許可済、係属中、放棄済

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Cheek, Jr., Reg. No. 33,367; Nils E. Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

私は、本出願の審査及び本出願に関連するすべてのビジネスに関わる手続きを米国特許商標局に対して遂行するため、共同でWENDEROTH, LIND & PONACK, L.L.P.法律事務所を構成しているMichael R. Davis (登録番号第25,134号)、Matthew M. Jacob (登録番号第25,154号)、Warren M. Cheek, Jr. (登録番号第33,367号)、Nils E. Pedersen (登録番号第33,145号)、Charles R. Watts (登録番号第33,142号) 及びMichael S. Huppert (登録番号第40,268号) 並びにカスタマー番号第000513号に付帯する他の弁護士及び弁理士を名いたします。

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from Takashima International Patent Office as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

私は、本願に関して米国特許商標局で行われるあらゆる手続行為に關し、ここに指名した米国弁護士を、弁護士と私の間で直接連絡をとることなく、(米国弁護士が連絡する相手先。譲受人もしくは日本の代理人等)からの指示を受けそれに従うことを、ここに承認します。指示を送る者が変更される場合は、その旨を上記米国弁護士は私から告知されます。

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Full Name of First Inventor 第一発明者の氏名	FAMILY NAME 姓名 <u>YOSHIMARU</u>	FIRST GIVEN NAME 氏名 <u>Masaaki</u>	SECOND GIVEN NAME ミドルネーム等の他の氏名
Residence & Citizenship 居住地及び国籍	CITY 市 <u>Chikujo-gun, Fukuoka</u>  Japan	STATE OR COUNTRY 州又は国名 <u>Japan</u>	COUNTRY OF CITIZENSHIP 国籍 <u>Japan</u>
Post Office Address 郵便物送付先	ADDRESS 住所 <u>c/o Yoshitomi Fine Chemicals, Ltd. Research Laboratory, 955, Oaza-Koiwai, Yoshitomimachi, Chikujo-gun, Fukuoka 871-8550 Japan</u>	CITY 市 <u>Japan</u>	STATE OR COUNTRY 州又は国名 <u>Japan</u>

2 - 00	Full Name of Second Inventor 第二発明者の氏名 KOHARA	FAMILY NAME 姓 KOHARA	FIRST GIVEN NAME 氏名 Masanori	SECOND GIVEN NAME ミドルネーム等その他の氏名	
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	Post Office Address 郵便物送付先 c/o Yoshitomi Fine Chemicals, Ltd. Research Laboratory, 955, Oaza-Koiwai, Yoshitomimachi, Chikugo-gun, Fukuoka 871-8550 Japan	ADDRESS 住所 c/o Yoshitomi Fine Chemicals, Ltd. Research Laboratory, 955, Oaza-Koiwai, Yoshitomimachi, Chikugo-gun, Fukuoka 871-8550 Japan	CITY 市 c/o Yoshitomi Fine Chemicals, Ltd. Research Laboratory, 955, Oaza-Koiwai, Yoshitomimachi, Chikugo-gun, Fukuoka 871-8550 Japan	STATE OR COUNTRY 州又は国名 Japan	ZIP CODE 郵便番号 871-8550
3 - 00	Full Name of Third Inventor 第三発明者の氏名 SHIBUYA	FAMILY NAME 姓 SHIBUYA	FIRST GIVEN NAME 氏名 Yoshifumi	SECOND GIVEN NAME ミドルネーム等その他の氏名	
	Residence & Citizenship 居住地及び国籍 Osaka-shi, Osaka	CITY 市 Osaka-shi, Osaka	STATE OR COUNTRY 州又は国名 Japan	COUNTRY OF CITIZENSHIP 国籍 Japan	
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I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

私は、私自身の知識に基づいて本宣誓書で私が行う表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明がすべて真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出版した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

1st Inventor Masaaki Yoshimaru Masaaki YOSHIMARU Date January 21, 2002
署名の日付
第一発明者（署名、ローマ字もしくは漢字）

2nd Inventor Masanori Kohara Masanori KOHARA Date January 21, 2002
署名の日付
第二発明者（署名、ローマ字もしくは漢字）

3rd Inventor Yoshifumi Shibusawa Yoshifumi SHIBUYA Date January 21, 2002
署名の日付
第三発明者（署名、ローマ字もしくは漢字）

The above application may be more particularly identified as follows:
上記出願は、さらには具体的には以下のように特定されます。

U.S. Application Serial No. _____ Filing Date _____
(上記出願番号) 提出の米国特許出願第 (上記出願番号) 号

Applicant Reference Number _____ Atty Docket No. _____
出願人側管理番号 (上記番号) 米国弁護士側管理番号 (上記番号)

Title of Invention _____
発明の名称